Edward Barton

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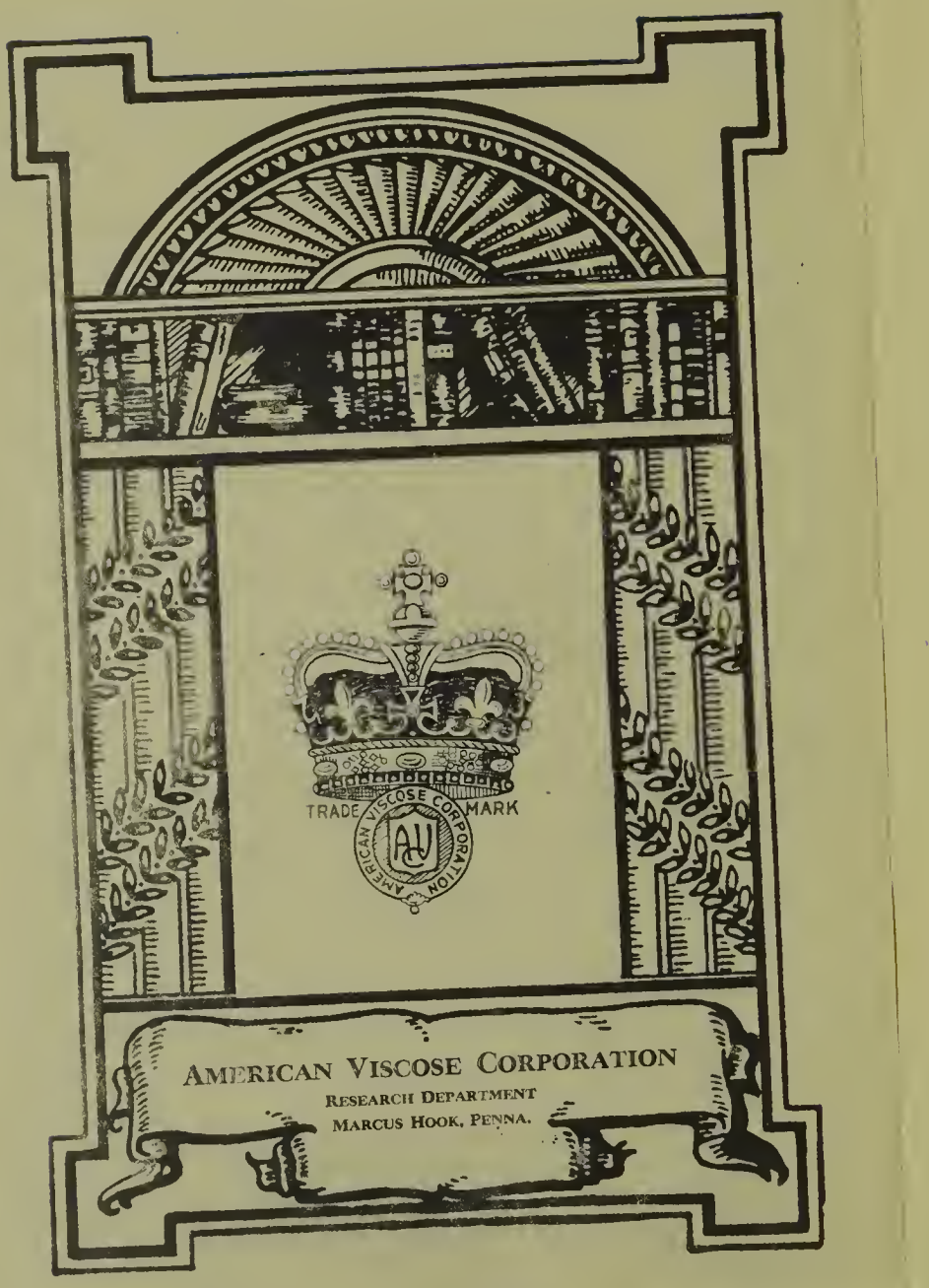

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# LABORATORY CORROSION TESTS

By W. S. CALCOTT and J. C. WHETZEL

Read and discussed at the Wilmington Meeting, June 22, 1923

## Introduction

Difficulties in chemical manufacturing are due not solely to the actual chemical process, but often to the difficulty of finding materials of construction of sufficient resistance to withstand the chemical and physical stresses of the operations and also prevent contamination of the product. The chemical resistance of a metal or its ability to withstand corrosion is, therefore, an important problem of chemical manufacture.

For the purposes of this report, corrosion of a metal may be defined as the reaction between the metal and another chemical compound by which a metallic product is formed which, possessing no mechanical strength, decreases the usefulness of the metal. The metallic compound may remain attached to the original metal as a coating or may be entirely removed from the metal, the result being the same in either case—a reduction in the amount of material of useful mechanical properties. Natural corrosion is the reaction between a metal and water. Chemical corrosion may be considered as including the reaction between the metal and a corrosive agent existing at any particular concentration. The mechanism is essentially the same in both cases. The present report is concerned with chemical corrosion solely.

Chemical corrosion data are of the greatest importance. Ability to make a proper choice of material for use in plant apparatus will often determine the success of an operation. These data must be not only qualitative, but also quantitative. It is not sufficient to know that one material will withstand the action of a given mixture better than another, but the comparative rates of deterioration must be known in order that the increased initial cost of one material may be balanced against the higher depreciation cost of another. In order to obtain these data, standardized methods of testing must be employed, together with intelligent application of the results to plant practice. Conditions within the plant must be observed in order that these may be duplicated in the laboratory. Such standard methods as have been adopted are included in the present report. If exact information is

available as to composition of the corrosive agent, concentration and temperature variations, impurities and movement of liquid within the apparatus, it is easily possible to determine the best metal for use before starting an operation, and thus predict not only the financial gain through decreased deterioration costs, but also the gain through the use of apparatus which will stand up and give continuous operation. Such information may also possibly determine the ultimate success or failure of a process.

The present report contains, in addition to methods of testing and interpretation of data, a discussion of the theory of corrosion. A bibliography of chemical corrosion, indexed in such a manner that it may be readily used as problems are encountered, and tabulations and summaries of the data on corrosion available at this laboratory are included.

## Summary

I. The tendency for corrosion of a metal by a solution depends upon (1) the potential effective for corrosion as determined by the combination of metal potential, overvoltage, and concentrations of metal and corroding ion; (2) the resistance offered by a protective coat; and (3) depolarization reactions removing hydrogen and protective products of corrosion.

II. The rate of the corrosion reaction varies as (1) area of metal computed from its linear dimensions, (2) rate of diffusion in corroding liquid, (3) saturation concentration of metal in corroding liquid, and (4) movement or velocity of corroding liquid. For a given set of conditions, the rate is constant in most laboratory experiments only after an initial time period (48 hrs.) has elapsed. The rate is increased greatly by increase in temperature, the logarithm of the rate varying as a straight-line function of the temperature for the range encountered in practice (20°–100° C.). More strictly, the logarithm of the corrosion rate is inversely proportional to the absolute temperature, as expressed by the following equation

$$\log R = A + \frac{B}{T},$$

where $A$ and $B$ are constants, $R$ the rate of corrosion, and $T$ the

absolute temperature. The simpler relation is, however, convenient for ordinary use.

III. A standard immersion corrosion test has been established for determining the rate of corrosion in solutions at rest expressed as inches penetration per month. All known factors affecting the results are described. A test for use with moving solutions, a review of electrochemical, microscopic, indicator, and vapor corrosion methods are contained in a discussion of corrosion measurement.

IV. Complete tabulations of corrosion data on file at this laboratory, a few extracts from the literature and a bibliography of chemical corrosion, arranged for use as specific problems arise, are attached.

V. The information necessary for determination of corrosion data and for its application to plant practice is listed and discussed. A brief outline of the use of materials against specific substances and for certain chemical operations is included. Methods of corrosion prevention are discussed in a general way.

## I. Theory of Corrosion

### *A. Tendency of Corrosion Reaction*

The driving forces of corrosion are almost entirely electrochemical, the electrochemical theory for natural corrosion having been generally accepted in this country. The fundamental requirement for corrosion is the presence of a solvent. If a solvent is present, the intensity of the action may be either great or small. The degree may be predicted to some extent by applying the general principles of electrolytic reactions.

Corrosion may be represented by an ionic reaction of the following type:

$$M + \overset{+}{H} = \overset{+}{M} + H.$$

The electrically neutral atom, $M$, interacts with the hydrogen ion, $\overset{+}{H}$, with the resultant production of a metal ion, $\overset{+}{M}$, which has taken up the hydrogen's electrical charge, depositing the latter as free hydrogen, $H$, on the surface of the metal. The type of reaction just described is the characteristic one for all cases of acid corrosion, which is by far the most important in chemical works. Of the cor-

rosion tests on file at this laboratory, about ninety-five per cent are concerned with acid corrosion. The remainder are chiefly basic, in which the metal forms an anion with an atom of oxygen, while hydrogen is liberated as before.

$$M + \overline{OH} = \overline{OM} + H$$

In any case, the metal goes into solution positively charged, resulting in the production of an electrostatic charge on the metal, preventing any appreciable corrosion unless this is neutralized through the formation of a complete voltaic cell, by flow of current through an external circuit. The latter may, however, be composed of two points of different potential on the metal itself caused by the non-homogeneous character of the surface.

The reversibility of the corrosion reaction is controlled by four primary terms composing it. In order to simplify the theoretical discussions, the acid reaction will be taken as the type, although the mechanism is essentially the same with any other. In the following restatement of the reaction, the determining factors are indicated under each component:

| | | |
|---|---|---|
| $M$ | $+$ | $\overset{+}{H}$ |
| I. Protective Coat.<br>II. Metal Potential. | | III. Hydrogen Ion Concentration = |
| $\overset{+}{M}$ | $+$ | $H$ |
| IV. Metal Ion Concentration. | | V. Overvoltage.<br>VI. Depolarization. |

These six factors determine the tendency for metal corrosion. In some cases, one factor may be so important that the rest are rendered negligible. This is true, however, of many common phenomena and should not be used as an argument against theoretical discussions of the corrosion reaction.

1. *Protective Coat.*—A coherent impervious film of an insoluble compound formed on the metal during the corrosion reaction will prevent perfect contact between the solution and metal, thus essentially removing the latter from the sphere of action. In order to prevent corrosion entirely, the film must be very dense and coherent. Often the protective film is an oxide, but all insoluble oxides formed

during the reaction are not necessarily protective. Porous iron rust will not protect against even atmospheric corrosion, but, by catalyzing the hydrogen removal, actually accelerates corrosion. Magnetic iron oxide will protect if it be continuous over the surface, but, if the metal is exposed, accelerates the reaction, since this oxide is electro-positive to iron. Aluminum is protected even against some of the strongest acids by its coat of oxide or basic compound.

The production of a protective coat may be developed into an important preventative of corrosion. By the addition of 0.05 to 0.25 per cent copper to the ladle before pouring steel, a metal resistant to acids is obtained, possibly through the formation of a protective oxide of copper. If sulphate ion is added to an acetic acid solution, the corrosive action against lead is lessened. A protective coat may also be formed through the differential corrosion of a metal, by which the material resistant to corrosion accumulates on the surface as corrosion proceeds, thus preserving the underlying metal.

The efficiency of a protective film or coat is determined largely by the concentration, temperature, and movement of the corroding liquid. In all cases the corrosion is increased as the solubility or removal of the protective coat is accelerated. A high concentration of sulphuric acid will dissolve lead sulphate, thus exposing metallic lead to corrosion, which will not occur at lower concentrations where the lead compound is insoluble. With aluminum the solubility of the coat, and consequently the corrosion, decreases with increasing concentration. Seligman and Williams [1] showed that the corrosion of aluminum by fatty acids reaches a minimum just before the water is entirely removed. When the anhydrous state is reached, the corrosion increases enormously. Water appears to be essential for the formation of the protective coat in this case. Increase in the temperature in general causes the removal of the protective film by solution. The concentration and temperature effects may usually be predicted by a consideration of the chemical character of the coating. If the liquid possesses considerable velocity across the metal surface, the protective coat is likely to be torn off mechanically, or its precipitation on the metal more or less prevented by rapid removal of the solution in contact.

2. *Metal Potential.*—The electrolytic potential or solution tension of the metal determines its affinity for the charged atom or ion pro-

[1] *J. Soc. Chem. Ind., 35,* 88 (1916).

ducing corrosion, and therefore is an important factor in determining its tendency to go in solution. Everything else being equal, for a homogeneous metal, the relative potential between the metal and solution would determine the corrosion rate. As a matter of fact, a homogeneous metal is never obtained in practice, and electrolytic action on the metal surface between points of different potential and the other corrosion factors are often of such importance that the potential may be neglected.

Gore [2] determined the relation between the voltaic current produced through an external circuit and the amount of corrosion. He found the weight of metal equivalent to the current produced varied from a few per cent to almost a hundred per cent of the total corrosion. The excess corrosion is caused by internal currents set up between electrodes formed on different parts of the metal surface itself. These differences exist upon nearly every surface, owing to the non-homogeneous chemical or physical character of the metal. The components of alloys will corrode differentially. A common example is the dezincification of brass. The selective corrosion of the iron-carbon alloys of steel has been noted often. The intergranular cement also corrodes in some cases more rapidly than the crystallized structure.[3] It is undoubtedly possible by simple surface treatments, such as cementation and case hardening, to produce steels resistant to corrosion in varying degrees. Stresses,[4] variations in structure by heat treatment,[5] and other purely physical effects will change the metal potential at points, resulting in the production of current. Although the potentials in these cases are very low, a large current flow with equivalent large corrosion will result because of the low resistance of the circuit. These anodic and cathodic points have been demonstrated by Walker and Cushman with indicators.

The normal value of a metal potential may be overcome by the production of the potentials in the circuit. Thus the important overvoltage effect after electrochemical action begins is equivalent to a lowering of the solution tension of the metal. The mechanism of passivity of metals is not entirely known, but the result is really the same as if the potential of the metal had been lowered. Corrosion by stray electric currents through the impression of an external elec-

[2] *Proc. Roy. Soc. London, 36,* 331 (1883).
[3] Ruder, *J. Ind. Eng. Chem., 5,* 452 (1913).
[4] Walker and Dill, *Trans. Am. Electrochem. Soc., 11,* 153 (1907).
[5] Eastick, *Metal. Ind., 11,* 524.

tromotive force is equivalent to a change in the solution pressure. Contact between two dissimilar metals will produce accelerated corrosion in an electrolyte.

Electrolytic corrosion is of special importance in chemical works. The intensity of the corrosion depends primarily upon the resistance in the external circuit and electrolyte. A very high corrosion over a broad area will result if the two metals are immersed in strong electrolytes of low resistance such as are encountered in chemical plants. Although the effective metal potential always determines the direction of electrolytic action between metals, it does not determine the real corrosion. Thus iron may be protected at the expense of zinc, but aluminum, although more electro-positive, does not protect because of its oxide coat, which renders it substantially inert.

An external electromotive force is not necessarily applied in such a direction as to increase the corrosion, but may be applied to its prevention by lowering the metal potential. This may be done either electrochemically by making electrical contact with a metal of higher potential or by making the metal to be protected the cathode through a direct current generator.[6]

Difference of potential of metals against solutions can not be determined absolutely, as a potential will exist at the other point of connection to the solution. By the use of standard normal electrodes fixing the concentration of metal ion in the solution relative values may be obtained. The series for the common metals against the normal hydrogen electrode ($H = 1$ mol liter, $P_{H_2} = 1$ atm.) in a solution containing one mol. of metal ion per liter is given below:[7]

| Metal | Ion | Potential volts |
|---|---|---|
| Aluminum | $Al^{+++}$ | +1.28 |
| Zinc | $Zn^{++}$ | +0.76 |
| Iron | $Fe^{++}$ | +0.43 |
| Lead | $Pb^{++}$ | +0.12 |
| Tin | $Sn^{++}$ | +0.1 |
| (Hydrogen) | $(H)^{+}$ | (0.0) |
| Copper | $Cu^{++}$ | —0.34 |
| Silver | $Ag^{+}$ | —0.79 |
| Gold | $Au^{+++}$ | —1.1 |

[6] Gee, *J. Soc. Chem. Ind., 32,* 521 (1913).

[7] Nernst, "Theoretical Chemistry," p. 806 (4th Eng. edition), and others.

Alloys show against a solution the potential of the less noble phase.[8] Some metallic compounds show potentials differing little from those of pure metals.

The tendency for solution is very great with metals high on the list and correspondingly low for those farther down. These relative values are, of course, influenced by the hydrogen and metal ion concentrations and may be completely overcome by the overvoltage.

3. *Hydrogen Ion Concentration.*—The effective potential producing corrosion is affected only by enormous changes in the hydrogen ion concentration. In most cases occurring in practice, sufficient change is not produced sensibly to affect the tendency for solution, caused by the metal potential. Thus, from the relation between electrical and chemical energy, the dependence of potential on concentration is given[9] by:

$$E = \frac{NRT}{F} \ln \frac{C_1}{C_2},$$

or at ordinary temperature (25° C.) for hydrogen

$$E = 0.059 \log \frac{C_1}{C_2},$$

in which $E$ represents the difference in potential in going from concentrations $C_1$ to $C_2$. Experimentally the range of hydrogen ion concentration has been shown to be from 10 molal in strong acid to $10^{-15}$ in strong alkali, making it possible to obtain a difference of about one volt. Since the relative potential of iron is only 0.6 volt, it is thus possible entirely to prevent its corrosion by the use of an alkaline solution. If the water in steam boilers is kept 0.03 normal with alkali, corrosion is entirely inhibited.

It has been demonstrated by Acree,[10] and others, that the addition of neutral salts gives a slight increase in the ionization of weak acids. The effect is so small, as shown by the logarithmic term, that the influence on corrosion is negligible. The enormous changes in hydrogen ion concentration, required for electrochemical effects, must not be confused with the important effect of concentration changes in the

[8] Bancroft, *Trans. Am. Electrochem. Soc., 3,* 297 (1903).
[9] Noyes and Sherrill, "General Principles of Chemistry."
[10] *Am. Chem. J., 41,* 457 (1909).

corroding liquid on the solubility of the products of corrosion, especially protective coats. Electrochemical considerations give tendencies, but whether the reaction will take place appreciably is determined by purely chemical factors.

4. *Metal Ion Concentration.*—The influence of the metal ion concentration is relatively unimportant and usually negligible in its effect on the solution tension of the metal in problems of corrosion. This concentration influences the metal potential according to the same function by which the hydrogen ion influences the potential of the hydrogen electrode. If the variations are of a very large order of magnitude, marked effects are produced as before. Thus iron will not displace copper in cyanide solution because of the low concentration of copper ion ($\overset{+}{Cu} = 10^{-19}$). Zinc may be plated out on one end of a zinc rod, immersed in saturated zinc chloride solution, while zinc will dissolve at the other end, immersed in water in contact with the chloride solution. These effects are caused directly by enormous differences in concentration of the metal ion.

5. *Overvoltage.*—No appreciable corrosion will take place without flow of current either between points of different potential on the metal surface or through an external circuit. As soon as the current begins to flow, a back electromotive force appears, thus reducing the potential effective for corrosion. This back electromotive force will continue to increase with resultant decrease in current flow until finally a decreased permanent current is obtained or electrochemical action stops almost entirely. This excess back electromotive force measured against the hydrogen electrode is the overvoltage, provided other disturbing factors are eliminated. In this case with hydrogen, the cathodic overvoltage is obtained. If oxygen is evolved at an anode, the anodic overvoltage is obtained. The overvoltage potential is a measure of the energy required to set free hydrogen after it has been deposited on or in the metal electrode.

From the data of Newbery,[11] the more common metals may be arranged in the order of their cathodic overvoltages in sulphuric acid as follows:

[11] *Mem. Proc. Manchester Lit. Phil. Soc., 61,* Parts II, III, Mem. No. 9, *C. A., 12,* 2496.

| Metal | Cathodic Overvoltage, $H_2$ in $H_2SO_4$ Solution |
|---|---|
| Zinc | 0.75 volt |
| Tin | 0.49 |
| Lead | 0.42 |
| Gold | 0.36 |
| Copper | 0.33 |
| Silver | 0.29 |
| Iron | 0.27 |
| Aluminum | 0.19 |
| Nickel | 0.24 |
| Platinum | 0.17 |

The higher the metal in the table, the more difficult it becomes to deposit hydrogen. Since hydrogen must be deposited before corrosion takes place, the higher the metal occurs in this list, the more resistance overvoltage offers to its corrosion.

Several striking illustrations are given above of the necessity of considering all the factors affecting corrosion. Zinc has a higher overvoltage than iron, but electrolytic action with the two in contact will result in corrosion of the zinc, since the actual combination with metal potentials in such a cell is sufficient to overbalance the high overvoltage of zinc. The zinc overvoltage makes itself felt at low hydrogen ion concentrations, thus zinc is not subject to atmospheric corrosion, although its metal potential is much higher than that of iron. For minimum corrosion the overvoltage should be high and the negative potential of the metal low.

Theoretically a metal will dissolve in acid only if the sum of its single potential and overvoltage is less than the single potential of a hydrogen electrode. Hadfield and Newbery [12] have made use of measurements of these quantities in predicting corrosion of steel. The methods of testing are complicated and slight errors will change entirely the order of corrosion, since the difference of two quantities of nearly the same magnitude is often considered.

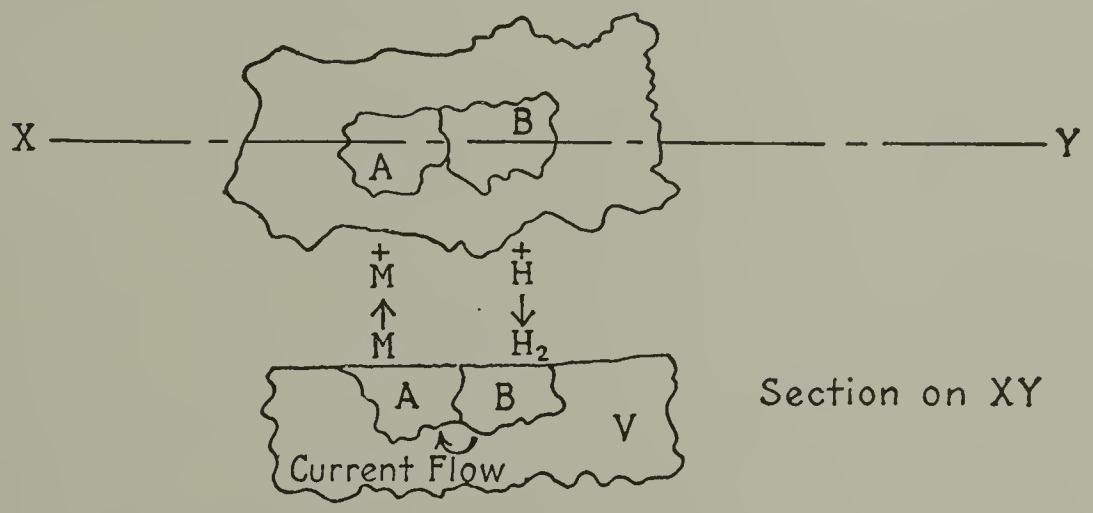
In addition to overvoltage at a point of gas evolution, an overvoltage effect is possible at any point where a change from ion to metal takes place. Measurements have been made of this potential. It is significant that the metal overvoltages are highest with nickel, iron, and cobalt. As these are also the metals most easily rendered passive, passivity may be related to a high metal overvoltage caused by rapid change from ion to metal.

[12] *Proc. Roy. Soc. London,* A93, 56 (1917); *C. A., 11,* 1814.

6. *Depolarization.*—The rapid removal of the products of corrosion, especially the deposited hydrogen, results in greatly accelerated corrosion. Any oxidizing agent will accelerate corrosion by removal of hydrogen through its oxidation to water. This type of depolarization is catalyzed also by the solid present; the metals of the iron group are catalysts. Catalytic action apparently varies inversely as the overvoltage. Zinc does not catalyze the removal reaction at all, which, with the difficulty of depositing due to overvoltage, prevents corrosion under ordinary conditions notwithstanding its high potential. Polarization is decreased by increase in temperature and rapid movement of the solution across the metal surface. It is also quite probable that corrosion is somewhat accelerated in a vacuum vessel because of the more rapid removal of hydrogen. However, the indications are that this vacuum effect is so slight as to be almost negligible (see data under velocity-corrosion effect).

## Summary

From the preceding discussions of the factors affecting the tendency for corrosion to take place, the conditions may be visualized and the effect of each factor more definitely established. If *A* and *B*




two points of different potential upon a metal surface, *A* being electro-negative to *B* and hence the anode, the *metal* (*M*) will dissolve at *A*, with the metal *ion* ($M^+$) passing into the main body of the solution unless an insoluble compound is formed by combination with an ion from the solution, in which case corrosion will be hindered or entirely prevented as soon as the *protective coat* becomes sufficiently

dense. The formation of $M^+$ with flow of current necessitates the deposition of the *hydrogen ion* ($H^+$) on the cathodic surface with formation of free hydrogen. If the metal surface is such as to produce a high *overvoltage* effect, the reaction will gradually decrease in intensity until the overvoltage potential reaches its equilibrium value. If the overvoltage is sufficiently high, corrosion may be practically stopped. In any case the effective potential, neglecting the effect of $M^+$ and $H^+$ concentrations on their respective electrodes, will be equal to the algebraic sum of the metal potential against the solution and the overvoltage. The removal of hydrogen or metallic products by *depolarization* with oxidizing or other agents will increase the rate of corrosion.

The conditions represented here may only last for a short period with a subsequent change of polarity due to the entire removal of the material acting as points of different potential, the uncovering of other material, or to the effect of the corrosion products. These reversals of polarity have been demonstrated by Cushman [13] and others with indicators.

Electrolytic considerations indicate the tendency for corrosion, but do not take into account many factors affecting the rate of the reaction, which is discussed in the section following.

### *B. Rate of the Corrosion Reaction*

1. *Diffusion Theory.*—Although a study of the rate of the corrosion reaction is complicated by initial electrochemical effects, disturbance due to gas evolution, and protective coat formation, a consideration from the viewpoint of rate of reaction in heterogeneous systems [14, 15] gives much valuable information.

Nernst [16] formulated from the work of Noyes and Whitney [17] the generalization that at the boundary between two phases, equilibrium is established with a practically infinite velocity compared with the rate of diffusion into or out of the saturated boundary layer.

[13] Cushman and Gardner, "Corrosion and Preservation of Iron and Steel."

[14] Nernst, "Theoretical Chemistry," p. 619 (4th Eng. edition).

[15] Lewis, "A System of Physical Chemistry. I. Kinetic Theory," p. 444 (2d ed.).

[16] *Z. Phys. Chem., 47,* 52 (1904).

[17] *Z. Phys. Chem., 23,* 689 (1897).

Thus, for the case of a metal and a liquid, if

$w$ = weight of metal corroded in time, $t$,
$w_1$ = weight of metal in saturated layer of liquid at surface of metal,
$w_2$ = weight of metal in main body of solution,
$v_1$ = volume of saturated layer of liquid,
$v_2$ = volume of main body of solution,
$c_1$ = concentration of metal in saturated layer of solution,
$c_2$ = concentration of metal in main body of solution,

then the rate of corrosion, $dw/dt = k(c_1 - c_2)$, in which $k$ is a velocity constant for the corrosion reaction.
Since,

$$c_1 = \frac{w - c_2 v_2}{v_1}$$

$$\frac{dw}{dt} = k\left(\frac{w - c_2 v_2}{v_1} - c_2\right) = k\left(\frac{w - c_2(v_2 + v_1)}{v_1}\right) \qquad (1)$$

Brunner [18] determined the thickness of film for several cases analogous to corrosion, the value remaining remarkably constant, averaging about 0.03 millimeter. For the volume of solution encountered in corrosion work, it can be readily shown that $v_1$ is negligible in comparison with $v_2$ for a thickness of saturated film of the order of magnitude of 0.1 millimeter, or sensibly $v_2 = v_2 + v_1$,
substituting in equation (1)

$$\frac{dw}{dt} = k\left(\frac{w - c_2 v_2}{v_1}\right)$$

But since $c_1 v_1 = w - c_2 v_2$,

$$\frac{dw}{dt} = k\, c_1 \qquad (2)$$

This result would have followed directly if $c_2$ were assumed negligible in comparison with $c_1$, but this is not apparent at first sight. It is also in accordance with Wilhelmy's law, which states that the velocity of a reaction is proportional to the concentration of reacting substance.
Now, if $A$ = area of metal exposed to corroding solution,

$D$ = diffusion coefficient of corroding solution, expressed in quantity of substance, which, during unit time, will

[18] *Z. physik. Chem., 47,* 56 (1904).

pass through unit sectional area, the concentration gradient being unity,

$S$ = thickness of saturated layer.

Then applying Nernst's theory of heterogeneous reaction velocity as experimentally confirmed by Brunner and others, the rate of corrosion may be expressed

$$\frac{dw}{dt} = \frac{AD}{S}(c_1 - c_2)$$

from which

$$k = \frac{AD}{S}$$

Equation (2) may now be rewritten

$$\frac{dw}{dt} = \frac{AD}{S} c_1$$

For any metal corroding in a given solution, $c_1$ is a constant determined by the equilibrium between the metal and solution. Thus, integrating,

$$w = \frac{AD}{S} c_1 t$$

the constant of integration dropping out, since $w = o$ when $t = o$.

Thus the corrosion will vary directly as the area of metal, diffusion coefficient of the solution, saturation concentration of the metal in solution and the time, and inversely as the thickness of the saturated layer. Brunner,[19] van Name and Edgar,[20] and Nernst and Merriam [21] have shown that the thickness of the saturated film depends upon the velocity of stirring the main body of the solution. Using an efficient paddle stirrer, they found the thickness to vary inversely as the 0.6 to 0.9 power of the rate of stirring. The indications from this data are that the corrosion will vary directly as a low power of the velocity. With metals and strong electrolytes, the power will probably be higher than with the dilute solutions used by these investigators, the protec-

[19] *Z. physik. Chem., 47,* 56 (1904).
[20] *Z. physik. Chem., 73,* 97 (1910).
[21] *Z. physik. Chem., 53,* 235 (1905).

tion afforded by protective coats and overvoltage probably decreasing greatly at high velocities.

It should be possible to demonstrate the dependence of the rate of corrosion upon the diffusion constant ($D$) of the solution and solubility ($c$) of the salt in the solution by proper choice of conditions. In one case, a metal must be exposed to the action of a pair of solutions, probably acids, both having the same ionization and same solubility for the metallic salt, but with diffusion constants differing as widely as possible. For another test, a metal and pair of solutions must be chosen so that the identical conditions are obtained for everything except the solubility, which should vary as much as possible. If such sets of conditions can be secured, considerable valuable information could be obtained upon the rate of the corrosion reaction by carrying on the parallel tests.

The value of the area, $A$, is not the true microscopic surface of the metal, but the value of the film area which is sensibly equivalent to the "quadratic dimensions." For this reason, very fine polishing is of little use in preparing test specimens for corrosion determinations.

2. *Concentration Effect.*—The effect of concentration of the corroding solution upon rate of corrosion is indicated in Table I and Figs. 1–5, Appendix, for simple aqueous solutions and for mixed solutions. The rate varies with the solubility of the metal or the product of corrosion in the solution. If the solvent producing solution is known and its concentration is plotted against the rate, a straight line should be obtained as indicated by preceding equation (2). The fact that the rate of corrosion of aluminum by strong nitric acid varies approximately as a straight line function of the water content of the acid has been demonstrated by Seligman and Williams.[22]

The peculiar effect of increase in corrosion rate of metals corroding in acid solution, by the addition of a salt of the metal to the acid, has been noted in this laboratory and by other observers. A slight increase in acid ionization with resultant higher hydrogen ion concentration, such as occurs with some acids under these conditions, can not account for this effect; a hydrogen ion concentration of a different order of magnitude must be produced in order sensibly to affect the electrode potential. A possible explanation exists in the

[22] *J. Soc. Chem. Ind., 35,* 665 (1916).

higher concentration of the products of reaction in the surface film, because of the additional solubility produced by a higher concentration of metal salt, or the removal of a protective coat by solubility in the salt solution. It is a fact that many metallic hydroxides are peptized and passed into colloidal solution in metallic salt solution. Although this increased corrosion rate is of great importance in considering the specific case of corrosion in acid solution containing metallic salts, it need not be considered ordinarily in corrosion work with ordinary acid solutions in the plant, since the main volume of the solution is sufficient to neglect concentration changes due to the progress of the corrosion reaction. However, a sufficiently high concentration of metallic salt may be produced in small pockets so that corrosion is seriously increased. For example, aluminum still heads, resistant to corrosion by acetic acid alone, are corroded rapidly if small pockets exist and an appreciable concentration of aluminum salt is allowed to collect over long periods.[23]

In the laboratory, the volume of test solutions must be made sufficient to prevent concentration changes due to the progress of the corrosion reaction.

Impurities in solution also have a great effect upon corrosion, undoubtedly due to their influence upon the saturation concentration of the reaction products. The influence of salts in acid solutions may usually be predicted by a consideration of the acid generated by interaction. Thus the addition of common salt to a sulphuric acid solution, with the formation of hydrochloric acid, produces far greater corrosion of lead, while the addition of a small amount of sodium sulphate to acetic acid decreases the rate of lead corrosion.

3. *Time Effect.*—The time required for initial effects to subside and the rate to become constant is indicated by the curves of Figs. 6 and 7, Appendix, which show the tendency for three different cases of corrosion. Evidently corrosion measurements for long time extrapolation should not be made until after this initial period. The error in three of the four cases due to averaging the rate from zero time to the time indicated in the plot is shown in Fig. 8, Appendix. For these three cases studied, an approximately true value of the rate may be obtained by measuring it between forty-eight and ninety-six hours. For the fourth case, aluminum in nitric acid, corrosion is

[23] Seligman and Williams, *J. Soc. Chem. Ind., 35,* 88 (1916); *36,* 409 (1917).

directly proportional to the time from the start. Thus, simple measurement from zero to forty-eight or ninety-six hours may give results 100 and 20 per cent high respectively. Although this initial time period of forty-eight hours has been established from only three sets of data, it is probable that these represent the maximum, and that in other instances a shorter time will be sufficient. Additional work should be carried out on this subject with more refinements, especially in regard to accurate temperature control.

If the product of corrosion must undergo a measurably slow reaction to be removed, diffusion alone will not determine the rate. If the main resistance is due to diffusion, increased movement of the liquid will increase the rate, but if the reaction at the metal boundary proceeds slowly, increased movement will have little effect. In any event, a theory which does not consider diffusion is incomplete.

4. *Temperature Effect.*—Temperature affects the rate of corrosion as well as the electrochemical tendencies for it to take place. For many homogeneous reactions the velocity is doubled for each 10° rise in temperature. With many heterogeneous reactions, where the rate is determined by diffusion, the velocity is increased about 1.5 times for the same rise. Temperature increases $D$, the diffusion coefficient, by lowering the viscosity of the solution. The smaller the initial diffusion rate, the greater the temperature coefficient. Thus hydrochloric and acetic acids have values of the diffusion coefficient [24] of 2.3 and 0.7 respectively for $4N$ acid, expressed in grams per day diffused through an area of one square centimeter down a concentration gradient of one gram per centimeter. The fractional increase for each ten degrees rise is 0.19 for hydrochloric and 0.28 for acetic acid.

Equations representing the increase in rate of reaction with temperature are largely empirical with little theoretical base. Arrhenius [25] and others have given such equations for the change of velocity constant of homogeneous reactions with absolute temperature, but none have been attempted for a reaction of the corrosion type. One article [26] was discovered in the literature in which the logarithm of the corrosion rate had been plotted against the temperature in order to make the low temperature rate appreciable on the diagram. Throughout a wide range the data followed approximately a straight line.

[24] Landolt Börnstein—Tabellen, 4th ed., p. 133.

[25] *Z. physik. Chem., 4,* 226 (1889).

[26] *J. Soc. Chem. Ind., 35,* 665 (1916).

No attempt was made to interpret this, although the relation is obvious. This relation has been found to hold in general, and makes a useful empirical rule, on account of the ease of plotting the data. The standard equation for the variation in the velocity of homogeneous reactions, namely,

$$\text{Log } R = A + \frac{B}{T},$$

has been found to hold also for the heterogeneous corrosion type of reaction. This equation, though less convenient to use, rests on a theoretical foundation, and can be used safely for extrapolation within reasonable limits.

### *C. Vapor Corrosion*

When corrosive vapors react with metals, the products of corrosion are not ordinarily removed. Even if no really protective coat is formed, the products will accumulate, covering the surface and increasing the difficulty with which the vapor can reach the metal, thus lowering the corrosion rate with time. For this reason, all vapor tests made so far are more or less unreliable for long time extrapolation, but the results are comparable, indicating in a general way the best material for use.

A study of the reaction rate at different time intervals would give data by which the rate could be calculated at any given time and the corrosion predicted closely.

## II. Corrosion Measurement

The general method usually employed for determining the rate of corrosion of materials consists in exposing specimens of the material to the action of the corrosive agent for a definite time and determining the loss in weight per unit area. No one has apparently tried to standardize a test of this type by measuring the influence of the numerous factors. An attempt has been made recently at this laboratory, and although many of the points need additional confirmation, it is felt that the methods described will give reasonable accuracy in the majority of cases.

### *A. Standard Corrosion Test with Solutions at Rest*

*Metal Test Piece.*—Size, 2″ x 1″ x 0.1″ (area = 4.6 sq. in.). Dimensions should be accurate to 0.01 inch in order to save time of

measurement and area calculation in the laboratory. Other shapes may be used within a range of ratio of length of edge to total area of test piece between 4 and 8. (See Table V, Appendix, for shape effect.)

*Preparation.*—The strip of indicated size may be cut from flat sheet metal or turned from pipe. Remove tool marks by successive use of file and emery. Exceedingly fine finishes are unnecessary, but the surface should be clean and reasonably smooth.

*Corroding Solution. Volume.*—Use 250 cubic centimeters per test piece of given area (4.6 sq. in.) for fairly rapid corrosion rate (0.01 inch penetration per month). The volume should be increased in proportion for pieces of greater area.

*Procedure.*—Place corroding solution in flask or wide mouth bottle and bring to temperature of test. Regulate this temperature to at least 1° C. in some type of rough thermostat. Suspend the weighed test piece upon a glass hook from a stopper of size to fit flask or bottle loosely and unaffected by corroding solution. Immerse test piece in solution when it reaches the proper temperature, closing the bottle or flask with the stopper. If the test is being made at a high temperature, a reflux condenser must be used, taking care to prevent condensate running directly on the test piece.

If the highest accuracy is required, expose one test piece for approximately forty-eight (48) hours and another for approximately ninety-six (96) hours. Remove from solution, wash thoroughly in a stream of water, and remove any coating. This cleaning may be done by dissolving off the coating (lead sulphate in ammonium acetate solution, lead chloride in hot water, etc.) or by rubbing and scouring with or without a soft powder as a mild abrasive. Do not adopt any method of cleaning until the error due to its use has been determined. Reweigh test piece after thoroughly drying, especially wiping out the hole by which it was suspended on the glass hook. From the loss during the last forty-eight hours, obtained by the difference in weight of the two test pieces, calculate the average rate of corrosion ($t = 48$ hrs.) as indicated under calculations.

Relatively good accuracy (results will be 20 per cent $\pm$ high) may be obtained in most cases by omitting the first measurement and averaging the rate over the entire period from zero to ninety-six hours. (See Fig. 8, Appendix.) The method to be used in any given test will depend upon the importance of the problem. Where

absolute quantitative data are necessary in balancing costs, the double determination should be made.

Run a check test simultaneously. Never place test pieces of different metals in the same container. It is permissible to place two pieces of the same metal in the same container, but they should not be in contact.

In case the metal develops pitting, this factor must be included in the results, since failure in any case will occur when a pit has entirely penetrated the metal. Determine the magnitude of this effect by grinding down on a metallographic grinding set until all the pits have just disappeared and solid metal is reached. The loss in weight during this grinding is determined and the pitting calculated as indicated.

*Calculations.*—

If $w =$ loss in weight in grams of test piece during immersion,
$A =$ area of test piece in square inches,
$s =$ density of metal in grams per cubic centimeter,
$t =$ time of exposure in hours,
then $C =$ rate of chemical corrosion expressed as inches penetration per month,

$$\frac{24 \times 30 \times w}{(2.54)^3 Ast} \quad \text{or} \quad C = 43.9 \frac{w}{Ast}$$

(A more logical factor for cost calculation would be expressed in pounds per square foot per year.)

In order to calculate the pitting corrosion, let $p =$ loss in weight in grams due to grinding out pits, then $D =$ rate of penetration of metal by both normal corrosion over the entire surface and local action due to pitting,

$$= 43.9 \frac{w + p}{Ast}$$

The depth of pitting or penetration due to pitting alone can not be determined from the grinding loss, but the degree of pitting may be indicated roughly by a pitting factor,[27] $P$.

$$P = \frac{C + D}{D}$$

[27] Aston and Burgess, *Trans. Am. Electrochem. Soc., 22,* 219 (1912).

In order to simplify calculations, $s$ for the more common metals has been substituted in the preceding equations for corrosion calculation with the following results:

| Metal | $s$ | C |
|---|---|---|
| Aluminum | 2.67 | $16.45 \frac{w}{At}$ |
| Copper | 8.9 | $4.93 \frac{w}{At}$ |
| Iron, Cast | 7.4 | $5.94 \frac{w}{At}$ |
| Lead | 11.4 | $3.85 \frac{w}{At}$ |
| Nickel | 8.8 | $4.99 \frac{w}{At}$ |
| Steel | 7.7 | $5.71 \frac{w}{At}$ |

*Conditions and Factors Affecting Results of Tests*

1. *Test Piece.*—Shape does not affect results within a reasonable range of ratio of length of edge to surface. (See Table V, Appendix.)

Fine polishing is unnecessary, although tool marks and oxide should be removed by rough treatment with emery. (See Table V, Appendix.)

2. *Volume of Corroding Solution.*—The effect of volume of corroding solution on rate of corrosion becomes practically negligible if a volume in excess of a certain minimum is used. (See Table V, Appendix.)

3. *Temperature of Corroding Solution.*—The temperature coefficient is high for all reactions, but in applying results to plant practice the works temperature would be estimated no closer than 1° C. For theoretical work in determining the law of temperature effect, it is absolutely necessary to use an accurately regulated thermostat. In comparing different metals care must be taken that the temperature is the same for all tests. (See Figs. 9 and 10 and Table IV, Appendix.)

4. *Time of Exposure of Metal to Corroding Solution.* The results of the corrosion test will vary enormously with the time of exposure. This variation is due to initial electrochemical surface

actions, such as overvoltage and to the period of time required for the formation of a protective coat. Both of these require time for reaching the equilibrium which will be maintained over a long time. Evidently initial effects of this kind must be neglected if a corrosion factor for use over a long period of time is to be obtained. The logical way is to measure the rate over an interval of time after the initial high corrosion rate has decreased and become constant. For the most careful work, this must be done. The experimental data, available at present, indicate that corrosion should be determined at the end of forty-eight and ninety-six hours. As a matter of fact, sufficient accuracy for comparative purposes may be obtained by omitting the first measurement and averaging the rate over the entire period. In the case of aluminum corroding in nitric acid, the weight of metal corroded per unit area is a straight line function of the time of exposure even for short periods. These data indicate that double determinations at different time intervals are not always necessary, but in any new case to be studied this will not be evident without testing. (See Tables II and III and Figs. 6, 7, and 8, Appendix.)

5. The magnitude of the error introduced in cleaning the test pieces is indicated for two representative cases in Table V, Appendix. This error exists only when one measurement is made; if two are made, the difference in weight neutralizes it.

### *B. Corrosion Test with Moving Solutions*

From the consideration of saturated films, protective coats, and overvoltage effects on the metal surface, it is evident that the movement of liquid across the surface affects the protection afforded by these factors. No quantitative relationship between the velocity of solution and rate of corrosion has been determined experimentally, notwithstanding the high velocities in actual operations. In order to make determinations of this character, a glass apparatus has been constructed in this laboratory by means of which corrosive liquids may be recirculated through a tube of the material, or across a metal test piece at definite velocities.

1. *Apparatus and Method for Corrosion Test under Velocity Conditions.*—A drawing of the apparatus used in velocity corrosion tests is given in Fig. 13 of the Appendix. The circulation of the corrosive liquid through the test tube and the return for recirculation is accomplished as follows:

The corrosive liquid is drawn from one large container ($K$) over the metal to be tested to another ($K_1$) by connection of the latter with a vacuum pump. When this container is filled, the vacuum is shut off by the action of a float ($F$) through the air valve ($A$) and a slight pressure applied, thus forcing the liquid back through the large return tube ($L$) to the lower container ($K$). When the level of the liquid in the upper container ($K_1$) and also the float chamber ($D$) is sufficiently lowered, the air pressure is cut off, connection with the vacuum supply again made, and the cycle repeated. With the vacuum on, flow of liquid through the return tube ($L$) is prevented by a check valve ($M$).

The test piece for high velocities is in the form of a tube ($T_1$, $T_2$), which is inserted in the system by means of glass reducers and heavy rubber connections. By the use of two sets of tubes of different diameter, check runs may be obtained for two different velocities. Tubes of $\frac{1}{16}''$ diameter are used for the highest velocity (2,000 ft./min. +). Two standard test pieces must always be placed at some point in the system to determine the static corrosion under the given conditions. This is most conveniently done by suspension on glass hooks in an overflow bottle ($Q$) connected to the large container by a glass syphon, the sluggishness of which prevents uncovering of the test pieces. Additional test pieces ($T_3$, $T_4$) for very low velocities (5–10 ft./min.) may be inserted in the large glass tubes on both sides of the metal test tubes. If these are inserted on the side nearest the vacuum container, they will be exposed under fairly high vacuum, which may accelerate the corrosion slightly.

*Procedure.*—Before insertion in the apparatus, the ends of the metal test tubes are coated with Bakelite enamel, baked on 24 hours at 100–150° C., the exposed metal surface thoroughly cleaned, and the tubes weighed. They are then ready to attach to the glass reducers by means of heavy rubber connections cut from rubber stoppers.

The metal air valve is greased, the proper quantity of corrosive liquid added to the large containers (about 20 liters), and connection made with the vacuum and air pressure supply through the screw clamps which regulate the velocity and rate of return of liquid. After the liquid begins to flow, the syphon between the float chamber and upper container is started and the flow through this regulated so that a certain lag exists in the height of liquid in the chamber, pre-

venting a stop of the float valve on dead center. The air valve must be oiled or greased every few hours. This must be done with the air pressure shut off from the apparatus or the oil will not be drawn down in the valve, but will be blown out the top by air leakage.

Since the flow over the test pieces is intermittent, the characteristic cycle of operaton must be obtained by time measurement with a stop-watch in order that the average velocity may be definitely determined. This necessitates the data indicated under *calculations*. The average time for each stop over a given number of hours is obtained by timing several representative cycles. The velocity for the given head is measured by noting the time required for a given volume to flow through a test-tube of known diameter.

*Calculations.*—

Let $t_m$ = time at maximum head $h$.
$t_0$ = time at zero head during discharge.
$t_a$ = time required to attain head, $h$, by rise from zero head, plus time required for decrease from $h$ to zero.
$T$ = total time of period to which measurements apply.
$T_0$ = time out for stops and shut-downs.
$T_v$ = actual time of period to be used in average velocity calculations.
$T_v = T - T_0 t_0$.

The average head may not be obtained by averaging $h$ directly, but $h$ may be averaged in this manner, since the velocity is proportional to the square root of the head for the conditions encountered in this apparatus.

Thus $\sqrt{\text{Average head during time liquid flows to upper container}}$

$$= \text{Av. max. head, } h\left(\frac{t_m}{t_m + t_a}\right) + \frac{\text{av. max. head, } h\left(\frac{t_a}{t_m + t_a}\right)}{2}.$$

$$\sqrt{\text{Average head during time liquid flows to upper container}} =$$

$$= \sqrt{\text{Average max. head, } h\left(\frac{2t_m + t_a}{2(t_m + t_a)}\right)}.$$

Since the square root of the average velocity head is now known, the actual head is readily obtainable. The velocity corresponding to this head is secured by noting the time required for a given volume of solution to pass through the test-tubes under the average head

maintained on the mercury manometer. If the velocity is known at about the same head, it may be obtained at the exact point by applying the square root relationship.

In the present apparatus, the lower container has been calibrated for ten liters of solution (syphon overflow bottle closed).

If $m =$ time in minutes for drop of level of liquid, from upper to to lower 10 l (calibration work),
and $d =$ inside diameter of tube in inches,
$v =$ velocity through tube in ft./min.,
then $=$

$$= \frac{10 \times 2.2}{62.4} \frac{1}{m} \frac{4 \times 144}{3.1416 \times d_a},$$

$$v = \frac{64.5}{md^2}.$$

For example, if

$d = 1''/10$ (small metal test tube) and
$m = 8$ min.
$v = 2{,}000 +$ ft./min.

If $d = 0.9''$ (large glass tube), then for the same value of $m$,

$$v = 7 \text{ ft./min.}$$

After the liquid has been circulated for a few days, all test pieces are removed, cleaned, weighed, and the weight of metal corroded per unit area $(w)/(a)$ for each test piece calculated. The total time at zero velocity $(t_0)$ is added to any time out for shutdowns $(T_0)$, and the static corrosion taking place during this period $(T_0 + t_0)$ calculated from the rate of corrosion of the pieces under static conditions. The results for this static period, expressed in grams per square inch, are subtracted from the loss for the whole period in the same unit and the loss during the actual time $(T - T_0 - t_0)$ liquid flowed through the test-tubes is obtained in grams per square inch. Since the loss in weight over a certain time period $(T - T_0 - t_0)$, within which the known average velocity was maintained has been determined, the rate of corrosion expressed in inches penetration per month, corresponding to this velocity, may be readily calculated as in the standard test for solutions at rest.

Thus, if $w_s$ = loss in weight during total time, $T$, of test piece immersed in solution at rest,
$A_s$ = area of test piece immersed in solution at rest,
$W_v$ = loss in weight in total time, $T$, of test piece subjected to moving solution,
$A_v$ = area of test piece subjected to moving solution,
$T$ = total time of test,
$T_0$ = total time out for shutdowns,
$t_0$ = total time that velocity across test piece is zero due to reversal of flow in apparatus,
$C_v$ = rate of corrosion expressed in inches per month during time ($T_0$) when liquid is moving across surface with average velocity, $v$,

$$C_v = \frac{43{\cdot}9}{sT_v}\left[\frac{W_v}{A_v} - \frac{W_s}{A_s}\left(\frac{T_o + t_o}{T}\right)\right].$$

An error will be introduced in the interpretation of results and in the determination of the quantitative relationship existing between velocity of liquid and corrosion by use of this intermittent apparatus. If the rate of corrosion is not proportional to the first power of the velocity, the direct averaging of velocities is not justified. The error probably will not be large, as the velocities averaged with the maximum are only correction terms. A constant flow apparatus similar in principle to the present one has been designed, but no attempt has been made to construct it. A high gravity flow tube with air lift would serve the same purpose, for solutions not affected by air.

Results should be interpreted by plotting the logarithm of the corrosion rate against the logarithm of the velocity. A straight line will be obtained if a power function exists. Very few data are available at present. The results of two runs are given below:

| Velocity Average ft./min. | Rate of Corrosion min./month | Notes |
|---|---|---|
| 1,460 | 0.0031 | |
| 8 | 0.0008 | 20″ vacuum |
| 8 | 0.0007 | atmospheric |
| 0.1 or less | 0.0007 | |
| 1,420 | 0.0025 | |
| 8 | 0.0006 | 20″ vacuum |
| 8 | 0.0005 | atmospheric |
| 0.1 or less | 0.0004 | |

2. *Velocity Corrosion Data.*—A number of velocity tests have already been carried out in this laboratory in the past, using methods other than those indicated. The results are indicated in Table VI, Appendix. Increase in velocity gave increased corrosion, but no definite relations were established. The following methods of testing were employed, the number used referring to the method given in the tabulation:

1. Gravity flow of solution across metal test pieces supported in glass tubes of varying diameters. Solution recirculated by air lift.

2. Test pieces attached to dish rotating in liquid.

3. Disk made of material to be tested, rotating in opposite direction to a wooden disk. Corrosion determined by cleaning and measuring thickness with micrometer.

4. Dropping liquid on metal test piece. Actually an impact test, but really gives qualitative indication of velocity effect.

### *C. Electrochemical Methods*

1. *Metal Potential Determination.*—The single potential of a given metal against any solution may be determined by combining it with another half cell of known potential through the proper solution, and balancing the electromotive force of the entire cell against a standard cell, by means of a wire bridge and capillary electrometer. Several combinations may be necessary in order to overcome the liquid potentials. Details may be found in any work on physical chemistry.

In simple tests of the potential existing between two metals in a given solution, the electromotive force of the combination should be balanced against a potentiometer. A millivoltmeter really measures the current and the resistance of the solution may not be negligible in comparison with that of the instrument. A number of determinations with the millivoltmeter are given in Table VII, Appendix. An initial potential must not be taken as indicative of continued electrolytic corrosion. A considerable electromotive force exists initially between aluminum and iron in concentrated nitric acid, but this gradually drops until it becomes negligible as far as affecting the corrosion rate.

If free energy data are available for the chemical change involved, the metal potential may be calculated. The obsolete method of calculation from the heat of reaction should not be used except where energy data can not be obtained. Calculation from heat data as-

sumes a zero temperature coefficient for the cell combination, which may be in error by a large amount.

2. *Overvoltage Determination.*—Newberry [28] describes fully a method of measurement by which the difference in potential between a metal when liberating hydrogen or oxygen and the respective hydrogen and oxygen electrode may be obtained. A large number of determinations have been made by the same investigator.[29] Hadfield and Newbery [30] have suggested the possibility of predicting corrosion of a metal in acid solution by comparing the sum of its single potential and overvoltage with the single potential of the hydrogen electrode.

3. *Mutual Corrosion Test of Metals.*—The electrolytic corrosion of two metals in contact in a solution is measured by the current flowing between the two. By immersing the two metals in the given solution and measuring the current flow through an external circuit of low resistance containing an ammeter, a quantitative idea of the electrolytic corrosion may be obtained. The loss in weight of the metal due to electrolysis may be easily calculated from the quantity of current by Faraday's law. The current will vary with the area of the test pieces, and the distance between them; these factors must be considered when comparisons are being made. The test must be continued until initial effects have disappeared and a constant current value has been obtained. Plant conditions must be followed as closely as possible, especially with regard to temperature and movement of liquid. Hanson and Lewis [31] have made use of this method in determining atmospheric corrosion.

A test in this laboratory of the mutual corrosion of aluminum and iron by this method demonstrated that the formation of a protective coat upon the aluminum effectively prevents electrolytic corrosion. A fairly high initial current flow rapidly decreased to zero as the protective effect of the coat made itself felt.

### *D. Microscopic Methods*

Desch,[32] Whyto,[33] and others have demonstrated the value of

[28] *J. Chem. Soc., 105,* 2420 (1914).

[29] *Proc. Roy. Soc. London, A93,* 56 (1917).

[30] *Mem. Proc. Manchester Lit. Phil. Soc., 61,* Mem. 9 (1917), C. A. *12,* 2496 (1918).

[31] *Trans. Am. Electrochem. Soc., 22,* 259 (1912).

[32] *J. Soc. Chem. Ind., 34,* 258 (1915).

[33] *J. Inst. Metals, 10,* 304 (1913); *11,* 235 (1914).

metallographic methods and the use of the microscope in indicating the mechanism of the corrosion of metals.

By examining the metal under a microscope before and after corrosion, the nature of the attack, comparative resistance of the different constituents, and texture of any adherent layers are determined. By stimulating corrosion with an externally applied electromotive force through a platinum cathode, an indication of the value of a metal may be obtained in a very short while. Application of these methods to the corrosion of brasses, by the investigators already mentioned, have given valuable results.

Metallography has been widely applied in studying the corrosion of the iron carbon alloys in steel. In fact, the ordinary methods of determining the different constituents by etching are merely selective corrosion tests. The corrosion of the intergranular cement in silicon iron alloys with exfoliation of the crystalline grains is an effect observed by Ruder.[34] In such a case, a mere immersion test would not determine the true loss in strength, since the amorphous material, giving strength to the metal, was almost entirely corroded away.

Microscopic comparison of the etching produced by the corrosive agent with that produced by standard etching solutions (alcoholic nitric acid, picric acid, etc.) will give information concerning the actual component of the metallic mass attacked. Decreased corrosion may be obtained by increasing the amount of most resistant material by heat treatment, or the addition or removal of certain constituents.

Photo-micrographs of protective metal coatings are of great value. They will determine the value of such coatings and the proper method of application. Rawdon, Grossman, and Finn [35] have applied metallography to the study of such metallic coatings, especially zinc.

The methods of preparing specimens for metallographic observations, including polishing, the use of etching solutions for determining constituents, and the technique of micro-photography, may be obtained from the numerous books on the subject.

### *E. Indicator Methods*

1. *Color Indicators.*—Points of different potential on metal surfaces, and microscopic voltaic couples such as are formed at uncovered points on metal coated material, may be distinguished by the use of indicators which change color when brought into contact with the

[34] *J. Ind. Eng. Chem., 5,* 452 (1913).
[35] *Chem. Met. Eng., 20,* 530 (1919).

products of the anodic or cathodic reaction. The ferroxyl reagent of Walker [36] is in general use for noting the solution of iron by means of ferricyanide in acid gelatin (50 g. gelatin, 450 g. water, 1 g. $K_3Fe(CN_6)$, 1 g. $H_2SO_4$), especially in determining the perfection of coated iron. The addition of phenolphthalein will locate the negative pole in some solutions, since the hydroxyl ions liberated will give the characteristic pink color of this indicator. The ferroxyl indicator may also be applied to determine whether iron in contact with another metal will corrode electrolytically. A simple test with this reagent will often save a more tedious electrical test.

If need arose, it would undoubtedly be possible to devise other indicators of value for use with other metals.

2. *Precipitation and Gas Evolution.*—Zinc coated metal may be tested for the amount of coating by determining the amount of another metal precipitated from solution or the time required for the precipitation. The Preece test makes use of a copper sulphate solution. Hydrochloric acid-antimony chloride [37] and basic lead acetate [38] solutions have also been used. A summary of such methods is given in a recent article by Rawdon, Grossmann, and Finn.[39]

The fact that iron in contact with zinc will liberate hydrogen in a hot caustic solution is the basis of another test for detecting pin holes and cracks in zinc coating.[40]

### *F. Vapor Corrosion Methods*

Vapor corrosion is determined by exposing standard test pieces to a stream of the corrosive vapor, measuring the loss in weight after removal of the coating and calculating the results as in solution tests. The method of generating the vapor will depend upon its composition, simple distillation in many cases being sufficient. If heat must be supplied for the generation, an electric hot plate should be used in order that the supply of vapor may be controlled closely. The test strips are contained in an electrically heated tube, which gives a uniform and easily regulated heat supply to prevent condensation. The temperature may be controlled with a rheostat, indications being fur-

[36] *J. Ind. Eng. Chem., 1,* 295 (1909).
[37] *J. Ind. Eng. Chem., 3,* 239 (1911).
[38] *Bull. Soc. Chim., 4,* I, 873 (Tambau).
[39] *Chem. Met. Eng., 20,* 458 (1919).
[40] *Proc. Chem. Soc. Testing Materials, 2,* 431 (1909).

nished by thermometers inserted in the tube. The details can not be fixed for all vapors, but the principle may be used.

A typical test of this character has been made with benzoic acid vapor at 250° C. on a large number of test pieces. The latter ($2'' \times 1'' \times 0.1''$) were distributed along the interior of a heated glass tube, about four feet long and 1⅛ in. in diameter, after it had been brought up to temperature by means of its electrical winding, consisting of 35′ of No. 22 Comet Resistance wire carrying about 8 amperes. After placing the strips, the vapor was turned into the tube and the test continued for about twelve hours. Vapor was supplied from a flask of boiling benzoic acid fitted with thermometer, large discharge tube, and resting upon an electric hot plate. The exit vapor from the long tube was kept at the same temperature as that of the vapor issuing from the flask. No selective corrosion in different parts of the tube was obtained.

Very little work has been done on the methods of testing vapors, but it is evident from what has already been said that the accumulation of the products of corrosion, which must take place at temperatures below that required for their volatilization, will cause a decrease in rate of attack as the time increases. No true values of the rate over long periods have been obtained, but the results are at least comparable, and will indicate the relative resistance of the metals tested.

## III. Corrosion Data

### *A. Literature*

Chemical literature contains considerable quantitative data on the corrosion of metals. In some cases the investigations have been very thorough and further work in these instances is unnecessary. For example, Seligmann and Williams have determined the action of nitric and organic acids on aluminum under practically every condition.[41] In general, all these data require calculation and rather close study before they can be applied to plant use. The labor of extracting all such data is too great for a report of this character, but the plan of making these abstracts, as definite problems arise, will be followed. For this reason a very complete bibliography (see Appendix) has been prepared with cross-references in order that the literature on a given case of corrosion may be readily available. This bibliography is intended to cover all the subject matter on chemical corrosion.

[41] *J. Soc. Chem. Ind., 35,* 88 (1916); *35,* 665 (1919); *36,* 409 (1917).

Additions will be made as subsequent work is produced and as better library facilities, especially on engineering subjects, become available. The aim is to produce a workable bibliography in order that long expensive testing may be saved. The corrosion of metals is essentially a problem of physical chemistry. Considerable data has been determined in this type of laboratory with great precision—far more than can be obtained in a chemical engineering laboratory. A large number of references are included on the factors affecting corrosion, especially those from the electrochemical point of view.

No attempt has been made to include all the references to natural atmospheric or water corrosion. All articles applying only to this type of corrosion have been omitted. Nevertheless, chemical and atmospheric corrosion are closely related and much subject matter of the latter type contains information of great value in chemical corrosion. For this reason, many references are included, which bear more or less directly on atmospheric and water corrosion. The same policy has been adopted with material concerning electrolytic corrosion, sea-water corrosion, corrosion in hot-water heating systems, and the prevention of corrosion. The bibliography is divided into the subheadings given below with cross-references wherever this has seemed desirable:

*Chemical Corrosion of Metals*
- Alloys, Special
- Alloys, Ferro
- Aluminum
- Brass
- Bronze
- Cadmium
- Chromium
- Copper
- Iron
- Iron and Steel
- Lead
- Metals, General
- Nickel
- Steel
- Tin
- Zinc
- Enamels, etc.

*Corrosion Factors*
- Metal Potential
- Overvoltage
- Electrolysis Solution Effect
- Rate of Corrosion Reaction

*Corrosion*
- General
- Tests and Methods
- Prevention
- Bibliographies

Results given in the literature are not calculated to the basis of inches penetration per month as used by this company, but data are usually available for this calculation. Conversion factors are given below for two cases already encountered. The nomenclature is the same as that used in calculations for the standard test.

| *Given* | *Required* | *Factor—Multiply by* |
|---|---|---|
| Grams/sq. in. in time, $t$..... | in. penetration/mo. | $4.39/st$ |
| Milligrams/100 sq. cm./24 hrs.... | in. penetration/mo. | $0.000118/s$ |
| | | 0.0000443 (aluminum) |

### *B. Jackson Laboratory Files*

All the data available at the Jackson Laboratory on specific cases of metal corrosion have been tabulated in Table VIII of the Appendix. A summary of data has also been prepared in Table IX, Appendix, from which the most important data for the corrosion of a metal in a given solution may be obtained without searching through the complete tabulation. Tables X, XI, and XII contain, respectively, the results of tests on corrosion by vapors, the corrosion of enamels and coatings, and the effect of immersion of different woods in dilute acid solution. The data recorded have been obtained from tests in this laboratory, and letters of information from the Eastern Laboratory and Experimental Station of this company.

Some record should also be kept of the performance of plant apparatus. Where rapid corrosion is taking place, measurement of metal thickness should be made and the results compared with laboratory tests.

## IV. Application of Corrosion Data to Plant Practice

### *A. Information from Plant*

Before a corrosion investigation is undertaken, a large sample of the corroding liquid, as it will actually exist in the plant, should be furnished unless the material is one of the common chemicals and may be secured from the laboratory chemical stock.

The following information should be furnished on a form when the request for an investigation is forwarded:

1. Type of apparatus.
2. Temperature range in apparatus.
3. Concentration changes in corroding liquid, due to both actual

changes produced during the process and those due to exposure of the atmosphere after draining.

4. Velocity of liquid in apparatus, rate of stirring, or data by which velocity may be approximated.

5. Impurities occurring in corrosive agent.

6. Cycle of operation including time of exposure of liquid per day.

7. Metals suggested from previous experience.

8. Metals which may possibly be in contact.

The influence of temperature, concentration changes, and contact with other metals has already been discussed, but little has been said concerning the effect of impurities and changes in concentration due to absorption or loss of water through exposure to the atmosphere. Small amounts of impurities will often produce great changes in the corrosion rate. If common salt reaches aluminum in contact with acid solution, the metal will corrode very rapidly because of its high solution rate in the hydrochloric acid formed. Arsenic in sulphuric acid decreases its action on iron by a large amount. Many other examples could be given, but these are sufficient to indicate the care that should be taken to test against the actual solution found in the plant. Changes in composition due to evaporation or absorption of moisture from the atmosphere, especially after draining a piece of apparatus, must be taken into account. An iron test piece immersed in concentrated sulphuric acid and exposed a few hours each day to saturated air showed almost three times the corrosion of another piece immersed in the acid continuously.

### *B. Specific Materials*

In considering the fitness of a material of construction for use in chemical works, corrosion is usually the largest factor. Mechanical strength is also important, but a weak material may be given sufficient rigidity by reinforcing it with a stronger one, while in general no practical method can be used to give a material chemical resistance. The effect of small amounts of corroded material in the final product must also be considered. In the manufacture of some organic materials, picric acid, for example, danger from explosion results if metallic salts are present. With other products, a lowering of quality is produced; for example, iron saddens many dyes, while lead condenser coils give phenol an objectionable yellow color.

A problem in corrosion starts with the corrosive agent or the operation. The result desired is a proper material for the container. In the following sections the best materials for use under the specified conditions are grouped first under the heading of the corrosive agent and second under the general chemical engineering operation involved. This information is based on data included in the present report, a few extracts from the literature, and in some cases from what is accepted everywhere as sound practice. The order of men-

1. Use with Corrosive Agents

| Corrosive Agent | | | Metals |
|---|---|---|---|
| Name | Concentration | Temperature | Resistant to Corrosion |
| | | ° C. | |
| Acetic anhydride..... | | 20–80 | Iron, copper, lead, aluminum |
| Acid, acetic..... | Glacial | 20–80 | Iron, copper, aluminum, lead |
| Acid, benzoic..... | Vapor | 250 | Nickel, copper |
| Acid, chloracetic..... | Plant | 20–100 | Nickel, lead, copper |
| Acids, fatty (propionic butyric, etc.)..... | Trace water | 100+ | Aluminum |
| Acid, hydrochloric ... | 10–30% | 20–80 | (Stoneware), special high silicon cast iron (special grades of Tantiron, Duriron, etc.), special hard lead |
| | 1–5% | 20–30 | (Stoneware), lead (especially hard lead) monel metal. |
| Acid, mixed..... | $HNO_3.H_2SO_4$ | | Mild steel, high silicon cast iron |
| Acid, nitric..... | 30–90% | 20–30 | Aluminum, high silicon cast iron (Tantiron, Duriron, Corrosiron, etc.) |
| | 30–90% | 50–80 | High silicon cast iron |
| | 10% | 20–80 | High silicon cast iron |
| Acid, sulphuric, fuming..... | 100+% | 20–100 | Cast iron, high silicon cast iron, steel |
| | 90–95% | 20–100 | Cast iron, high silicon cast iron, steel, hard lead |
| | 10–25% | 20–30 | Lead, nickel, special high silicon cast iron |
| | 10–25% | 80–100 | Special high silicon cast iron |
| | 1–5% | | Lead, brass, bronze, monel metal. |
| Acid, sulphurous..... | Strong | 20–100 | Lead, bronze |
| Benzaldehyde..... | Plant | 20–30 | Zinc, (drum containers) |
| Caustic, mixed | KOH/NaOH = 10/7, 25°–50° Bé. | 100+ | Cast iron (not too high in Si), steel |
| Caustic, soda..... | 40–5 −° Bé. | 20–100+ | Cast iron (not too high in Si), steel |

1. USE WITH CORROSIVE AGENTS.—*Continued*

| Corrosive Agent | | | Metals |
|---|---|---|---|
| Name | Concentration | Temperature | Resistant to Corrosion |
| Dyes: | | | |
| Alizarine paste..... | +1–2% HCl | 100+ | Monel metal |
| Magenta solution.. | | 20–100 | Iron |
| Malachite green mother liquor ... | | 20–80 | Lead, brass |
| Pontachrome brown, MW. paste..... | | 50–80 | Cast iron |
| Pontachrome brown, 3a, paste..... | | 50–80 | Cast iron (dye slightly dull) |
| Gases and vapors: | | | |
| Benzoic acid vapor. | | 250 | Nickel, copper |
| Chlorine..... | Dry | 20–80 | Iron, steel |
| | | 100+ | High silicon cast iron |
| Sulphur dioxide.... | Dry | 20–500 | Cast iron |
| | Moist | 20–200 | Lead |
| | Moist | 200–500 | Cast iron |
| | Dry | boiling | Cast iron, steel |
| Mono-nitrochlor-benzol—moist.... | | boiling | Brass |
| Intermediates: | | | |
| Chlorbenzol..... | | | Iron, steel |
| Brown acid mother liquor..... | | 20–80 | Lead |
| H-acid nitration mixture..... | | 100 | Lead (rather high corrosion) |
| Koch's acid..... | | 20–80 | Lead |
| Oxy acid, 1 : 5..... | | 20–30 | Lead (rather high corrosion) |
| p-nitrophenol..... | | 20–100 | Lead |
| Phenylglycine mother liquor, ferrous... | | 20–80 | Iron |
| Salts: | | | |
| Sodium hydrosulphite..... | 20% | 20–30 | Lead |
| Sodium hypochlorite..... | 20% | 20–30 | Cast iron, steel |
| Sodium sulphide... | 5–25% | 20–100 | Lead |

tion indicates in general the relative resistance to corrosion, the material least corroded usually appearing first. If a common metal can be used with very little increased corrosion, over an expensive special alloy, the latter evidently will not receive first choice; in fact, if the cost is too high, it may not be on the list at all. Non-metals, such as stoneware, are only mentioned where nothing else is possible or conditions make it highly desirable for their use.

2. Use in Chemical Operations

| Operation | Metal |
|---|---|
| Caustic kettles and autoclaves | Cast iron |
| | Cast steel (high pressure) |
| | Silver lined for special use |
| Caustic fusions | Cast iron (low silicon and 2–5% manganese best) |
| Chlorination: | |
| Dry chlorine lines | Iron, steel |
| Moist chlorine lines | (Earthenware) (enamel or asphalt lined) |
| Chlorinators | Cast iron, lead, enamel, steel, nickel, copper. |
| Distillation: | |
| Acetic acid, glacial | Copper, aluminum, high silicon cast iron |
| Fatty acids (propionic, butyric, etc.) | Aluminum |
| Nitric acid | High silicon cast iron, silica |
| Organic acid materials | Nickel, copper, silver lined iron and steel |
| Phenol | Cast iron, silver lined |
| Filtrations: | |
| Strong acids | Filtros |
| Weak acids | Monel metal cloth, filtros |
| Alkalies | Monel metal cloth |
| Electrolytic cells: | |
| Diaphragms: Alkaline liquors | Asbestos, alumina |
| Acid and Neutral liquors | Filtros |
| Electrodes: Product desired and surface considerations rather than corrosion are determining factors. | |
| Dye containers | Nickel, copper, enameled metal, wood. |
| Nitrations: | |
| Nitrators: Mixed acid | Steel, high silicon cast iron, lead, enameled metal |
| Strong nitric acid, low temperature | Aluminum |
| Fume lines | Aluminum, stoneware |
| Denitrating recovery systems | Stoneware, high silicon cast iron |
| | Lead |
| Reductions | Cast iron, lead |
| Sulphonations | Cast iron, lead |

3. *General Notes.*—The impurities in iron and steel and the addition of other metals have a considerable effect on the rate of corrosion. Copper in small amounts (1 per cent or less) increases the resistance to acids. Phosphorus and sulphur may increase the corrosion if present in sufficiently large amounts. Manganese in the usual quantity has little effect. High silicon (20 per cent +) cast irons are very resistant; this quality is very much increased by the addition of metals such as nickel and copper. Graphitic carbon probably protects cast iron somewhat by forming a protective coat as the corrosion progresses. Strong nitric and fuming sulphuric acid appear to penetrate cast iron without corroding the mass of the metal; the structure is very much weakened in such cases, making it unsafe for pressure vessels.[42]

[42] *J. Soc. Chem. Ind., 38,* 31T (1919).

For certain weak acids and in operations where metals introduce objectionable impurities, wood is very useful. Hard woods in general give the best service. Cypress and hard maple are excellent, but the latter is expensive. California red wood has come into considerable use. Chemical stoneware can be used with almost any acid. Alkalies attack both woods and stoneware. Brasses, bronzes, and special alloys such as monel metal are very useful against weak acids. Enameled steel is similar to stoneware in its properties, but rather fragile. Where considerable stress is encountered, as, for example, with stirrers, enameled steel may be preferable to cast iron. Steel alone should not be used with cast iron because of danger from electrolytic action.

## Corrosion Prevention

A material non-resistant to corrosion may be protected by:

*A.* Application of a coating to the surface.
*B.* Additions during process of manufacture forming an integral part of the material.
*C.* Electrochemical means.

Among the different types of coating may be mentioned:

1. *Paints.*—A complete discussion of this subject is contained in Cushman and Gardner, "Corrosion and Preservation of Iron and Steel." Asphalt paints are especially useful in chemical works.

2. *Metallic Coatings.*—Metals may be applied to a surface either electrolytically or by dipping in a molten bath. Zinc and tin are the more common metals used for protection, especially against atmospheric corrosion. Galvanized and tinned metals are of little or no use in chemical plants for preventing corrosion. Tin is useful against alkalies and both tin and zinc coated metals are made use of where danger from contamination with other metals is present, particularly in protecting dyes and textile chemicals from contact with iron. Practically no tinned metal is perfectly coated, resulting in greatly accelerated corrosion at exposed spots. There is no reason why other metals, especially nickel, should not be used as protective coats against actual chemical corrosion in some instances. Silver lined autoclaves and stills are fairly common. Aluminum applied to iron by the calorizing process [43] protects against oxidation or high

[43] *Trans. Am. Electrochem. Soc., 27,* 253 (1915).

temperature corrosion by air. Silicon tetrachloride in contact with iron at high temperatures deposits metallic silicon upon the surface of the latter.[44] The high resistance of silicon to reagents at once suggests the use of such a process in giving a chemical resistant material.

3. *Enamels.*—Glass enameled chemical apparatus is in more or less common use at present. It is rather fragile, requiring some care to prevent chipping due to temperature changes and mechanical handling. Enamels of this type vary considerably in their resistance against different chemicals. Corrosion tests should always be made. Glass enamels are, of course, not used against alkalies. A certain class of enamels (Bakelite,[45] sodium silicate, etc.) may be applied as a liquid varnish and then baked at a moderately low temperature. They are fairly resistant, but brittle. An inert filler may frequently be used to advantage with this class of enamels.

4. *Protective Oxides.*—The protection afforded iron by a continuous coating of magnetic oxide has been made use of by Barff, Bower, Well, and others who produce an artificial coating of this type by passing steam or gases over the hot metal. A discontinuous coat will accelerate the corrosion of exposed metal.

5. *Protective Linings.*—By the attachment of thin plates of resistant material of low mechanical strength to a supporting framework of strong metal, a satisfactory container is sometimes obtained. Lead lined tanks and pipes are frequently used. Ebonite or hard rubber has been vulcanized on steel for use with hydrochloric acid.[46]

The disadvantage of all surface coating methods is the difficulty of obtaining a perfect coat covering the entire surface. Subsequently considerable care is required to keep this coating continuous. It is far better to use a single homogeneous material.

A large number of alloys are much more resistant to corrosion than single metals. Small additions during the process of manufacture may increase the resistance greatly. The lessened corrosion of steel containing copper has already been mentioned. The same metal or nickel added to high silicon cast iron increases the already high resistance of the latter. Nickel is especially useful as a component of alloys with low corrosion rates.

[44] *Chem. Trade J., 64,* 99 (1919).
[45] *Trans. Am. Electrochem. Soc., 15,* 593 (1909).
[46] Brit. Pat. 124997, British Dyes, Ltd.

A metal may also be protected by decreasing its effective potential against the corroding solution. This may be accomplished by contact with a more electro-positive material, or by making the metal to be protected the cathode by proper connections with a direct current generator and suspended anode. The latter has not been used in practice, and the former would be of little use in protecting chemical apparatus, although it has had some application in the prevention of boiler corrosion. Inhibitive paints, protecting because of the electrochemical character of the pigments, and useful in cases of atmospheric corrosion, would also be of little use for prevention of chemical corrosion. (See page 142 for discussion.)

# APPENDIX

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FIGURES—GRAPHICAL INTERPRETATIONS

FIG. 1. Effect of Concentration upon Corrosion of Aluminum by Nitric Acid.

FIG. 2. Effect of Concentration upon Corrosion of Aluminum by Mixed Acid.

FIG. 3. Effect of Concentration upon Corrosion of Aluminum by Acetic Acid.

FIG. 4. Effect of Concentration upon Corrosion of Mild Steel by Dilute Mixed Acid.

FIG. 5. Effect of Concentration upon Corrosion of Lead by Dilute Mixture of Sulphuric and Hydrochloric Acid.

FIG. 6. Effect of Time of Exposure upon Corrosion.

FIG. 7. Effect of Time of Exposure upon Corrosion (Long Time).

FIG. 8. Effect of Time of Exposure in Laboratory Test upon Rate of Corrosion Results.

FIG. 9. Effect of Temperature upon Rate of Corrosion of Aluminum in Nitric Acid (Sp. Gr. 1.42).

FIG. 10. Effect of Temperature upon Rates of Corrosion of Cast Iron, Lead, and Steel in Hydrochloric Acid (10 per cent).

FIG. 11. Effect of Temperature upon Log Rate of Corrosion of Aluminum in Nitric Acid (Sp. Gr. 1.42).

FIG. 12. Effect of Temperature upon Log Rate of Corrosion of Cast Iron, Lead, and Steel in Hydrochloric Acid (10 per cent).

## TABULATION OF CORROSION DATA

### *Notes on Tabulations*

*Method Number.—*

1. Standard Jackson Laboratory test.
2. Older tests, time of exposure, and volume of solution low. Results are probably high in most cases.
3. Very old data or conditions unknown.

*Reports of Data.—*

J—Jackson Laboratory Corrosion File.
C—Jackson Laboratory Card File for Corrosion Data.
E—Eastern Laboratory.
S—Experimental Station.

Temperature effect recorded in separate table (Table IV) if determinations were made at more than two temperatures.

Velocity effect recorded in separate table (Table VI).

Hardness (H) measured with Shore scleroscope.

## TABLE I

### Effect of Concentration of Corroding Solution upon Rate of Corrosion

| Metal: Aluminum[46] Solution: Nitric Acid Temperature: 20° C. | | Aluminum[46] Mixed Acid 20° C. | | | Aluminum[46] Nitric Acid 25–30° C. | |
|---|---|---|---|---|---|---|
| Conc. $HNO_3$ % by Wt. | Rate of Corrosion. Inches Penetration per Month | Conc. $H_2SO_4$ % by Vol. | $HNO_3$ % by Vol. | Rate of Corrosion. Inches Penetration per Month | Conc. $HNO_3$ % by Wt. | Rate of Corrosion. Inches Penetration per Month |
| 99–100 | 0.000005 | 100 | 0 | 0.0054 | 40 | 0.0087 |
| 96.1 | 0.00002 | 90 | 10 | 0.0077 | 50 | 0.0080 |
| 90.8 | 0.00013 | 80 | 20 | 0.0078 | 60 | 0.0052 |
| 89.0 | 0.00044 | 70 | 30 | 0.0079 | 70 | 0.0031 |
| 69.6 | 0.00133 | 60 | 40 | 0.0079 | | |
| 55.8 | 0.00177 | 50 | 50 | 0.0078 | | |
| 40.7 | 0.00244 | 40 | 60 | 0.0075 | | |
| 22.2 | 0.00310 | 30 | 70 | 0.0068 | | |
| 9.3 | 0.00133 | 20 | 80 | 0.0051 | | |
| 4.4 | 0.00088 | 10 | 90 | 0.0033 | | |
| | | 0 | 100 | 0.0007 | | |

| Metal: Aluminum[47] Solution: Acetic Acid Temperature: 20° C. | | Aluminum[47] Acetic Acid Boiling | |
|---|---|---|---|
| Conc. % Acetic Acid | Rate of Corrosion. In. Penetration per Month | Conc. % Acetic Acid | Rate of Corrosion. In. Penetration per Month |
| 99.2 | 0.00000 | 99.9 | 0.00031 |
| 90 | 0.00001 | 98 | 0.00155 |
| 60 | 0.00003 | 90 | 0.00732 |
| 10 | 0.00004 | 80 | 0.01307 |
| 1 | 0.00005 | 70 | 0.01461 |
| 0.5 | 0.00006 | 60 | 0.01805 |
| 0.25 | 0.00008 | 50 | 0.01849 |
| 0.1[48] | 0.00010 | 40 | 0.02180 |
| 0.02[48] | 0.00014 | 20 | 0.02360 |
| 0.004[48] | 0.00004 | 10 | 0.02578 |
| | | 5 | 0.02700 |
| | | 1 | 0.05320 |
| | | 0.2 | 0.03410 |

[46] Data calculated from Seligman and Williams, *J. Soc. Chem. Ind.*, *35*, 665 (1916).

[47] *J. Soc. Chem. Ind.*, *35*, 88 (1916); *36*, 409 (1917).

[48] 10–15° C. temperature.

| Metal: Mild Steel<br>Solution: Dilute Mixed Acid<br>Temperature: 25° C. + | | | Lead<br>Dilute Mixture of $H_2SO_4$ & HCl<br>25° C. + | | |
|---|---|---|---|---|---|
| Conc. % $H_2SO_4$ | % $HNO_3$ | Rate of Corrosion. In. Penetration per Month | Conc. % $H_2SO_4$ | % HCl | Rate of Corrosion. In. Penetration per Month |
| 20 | 0 | 0.251 | 20 | 0 | 0.0001 |
| 18 | 2 | 2.802 | 18 | 2 | 0.0032 |
| 15 | 5 | 8.38 | 15 | 5 | 0.0179 |
| 10 | 10 | 11.32 | 10 | 10 | 0.0489 |
| 5 | 15 | 9.52 | 5 | 15 | 0.0856 |
| 2 | 18 | 8.56 | 2 | 18 | 0.1326 |

## TABLE II

### Effect of Time of Exposure upon Corrosion

| Metal: Mild Steel<br>Solution: Conc. Commercial $H_2SO_4$ (93%)<br>Temperature: 22–27° C. | | Mild Steel<br>Sodium Hydrosulphite (20%) Conc.<br>22–27° C. | | Mild Steel<br>Com. $H_2SO_4$ (93%)<br>22–27° C. | |
|---|---|---|---|---|---|
| Time of Exposure $t$ in hr. | Wt. of Metal Corroded per Unit Area $\frac{W}{A}$ in $\frac{\text{Gr.}}{\text{sq. in.}}$. | Time of Exposure $t$ in hr. | Wt. of Metal Coroded per Unit Area $\frac{W}{A}$ in $\frac{\text{Gr.}}{\text{sq. in.}}$. | Time of Exposure $t$ in hr. | Wt. of Metal Corroded per Unit Area $\frac{W}{A}$ in $\frac{\text{Gr.}}{\text{sq. in.}}$. |
| 1.0 | 0.0054 | 1.0 | 0.0270 | | |
| 3.0 | 0.0068 | 3.0 | 0.0358 | | |
| 6.2 | 0.0112 | 6.25 | 0.0398 | | |
| 26.7 | 0.0334 | 25.0 | 0.0495 | | |
| 20.0 | 0.0216 | 26.75 | 0.0312 | 20.0 | 0.0157 |
| 49.5 | 0.0280 | 51.0 | 0.0309 | 49.5 | 0.0215 |
| 67.75 | 0.0255 | 70.25 | 0.0362 | 67.75 | 0.0254 |
| 91.5 | 0.0436 | 93.25 | 0.0398 | 92.5 | 0.0360 |
| 145.5 | 0.0459 | 147.0 | 0.0467 | 145.5 | 0.0516 |
| 216.0 | 0.0530 | 195.0 | 0.0537 | 216.0 | 0.0667 |
| 409.5 | 0.1241 | 411.0 | 0.1308 | 409.5 | 0.1080 |
| 727.0 | 0.2418 | 728.4 | 0.3826 | 716.5 | 0.1550 |
| 1,028.5 | 0.1799 | 1,030.0 | 0.6000 | 1,028.5 | 0.1996 |
| | | | | 2,665.5 | 0.3330 |

Metal Aluminum, Solution 30% $HNO_3$, Temp. 27° C. ± 1°.

| Time of Exposure t in Hrs. | Wt. of Metal Corroded per Unit Area. $\frac{W}{A}$ in $\frac{\text{Gr.}}{\text{sq. in.}}$ |
|---|---|
| 18.5 | 0.0135 |
| 24 | 0.0173 |
| 44 | 0.0287 |
| 88.5 | 0.0661 |
| 163.5 | 0.1332 |

## TABLE III

### Effect of Time of Exposure in Laboratory Test upon Rate of Corrosion Results

| Metal: Mild Steel<br>Solution: Conc. Com. $H_2SO_4$ (93%)<br>Temperature: 22–27° C. | | Mild Steel<br>Sodium Hydrosulphite (20%)<br>$Na_2S_2O_4$ 95%<br>22–27° C. | | Mild Steel<br>Conc. Com. $H_2SO_4$ (93%)<br>22–27° C. | |
|---|---|---|---|---|---|
| Time of Exposure hr. | Rate of Corrosion. Inches Penetration per Month. | Time of Exposure hr. | Rate of Corrosion. Inches Penetration per Month. | Time of Exposure hr. | Rate of Corrosion. Inches Penetration per Month |
| 1.0 | 0.0308 | 1.0 | 0.1540 | | |
| 3.0 | 0.0129 | 3.0 | 0.0681 | | |
| 6.2 | 0.0103 | 6.25 | 0.0377 | | |
| 26.7 | 0.0071 | 25.0 | 0.0113 | | |
| 20.0 | 0.0062 | 26.75 | 0.0067 | 20.0 | 0.0047 |
| 49.5 | 0.0032 | 51.0 | 0.0035 | 49.5 | 0.0026 |
| 67.75 | 0.0021 | 70.25 | 0.0029 | 67.75 | 0.0021 |
| 91.5 | 0.0027 | 93 25 | 0.0024 | 92.5 | 0.0023 |
| 145.5 | 0.0018 | 147.4 | 0.0018 | 145.5 | 0.0021 |
| 216.0 | 0.0014 | 195.0 | 0.0016 | 216.0 | 0.0018 |
| 409.5 | 0.0017 | 411.0 | 0.0018 | 409.5 | 0.0016 |
| 727.0 | 0.0019 | 728.0 | 0.0030 | 716.5 | 0.0013 |
| 1,028.5 | 0.0010 | 1,030.0 | 0.0033[49] | 1,028.5 | 0.0012 |
| | | | | 2,665.5 | 0.0007 |

Metal Aluminum, Solution 30% $HNO_3$, Temp. 27° C. ± 1°.

| Time of Exposure hr. | Rate of Corrosion Inches Penetration per Month |
|---|---|
| 18.5 | 0.0120 |
| 24 | 0.0119 |
| 44 | 0.0107 |
| 88.5 | 0.0123 |
| 163.5 | 0.0134 |

[49] Total rate, pitting corrosion included, = 0.0046 in/mo.

TABLE IV

EFFECT OF TEMPERATURE UPON RATE OF CORROSION

| Metal | | Solution | | | Method No. | Rate of Corrosion Inches Penetration per Month |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | | |
| Copper | | P-Nitro phenol | Saturated solution | 0 | 2 | 0.00003 |
| " | | " " | " " | 40 | " | 0.00037 |
| " | | " " | " " | 60 | " | 0.00040 |
| " | | " " | " " | 100 | " | 0.00062 |
| Iron | Cast, soft, hardness = 8 | Acid, hydrochloric | 10% | 25 | " | 0.4381 |
| " | do. | " " | " | 40 | " | 0.6886 |
| " | do. | " " | " | 50 | " | 0.8089 |
| " | do. | " " | " | 60 | " | 1.0140 |
| " | do. | " " | " | 70 | " | 1.2615 |
| " | do. | " " | " | 80 | " | 1.5202 |
| " | do. | " " | " | 90 | " | 1.7606 |
| " | do. | " " | " | 110 | " | ..... |
| Lead | | Acid, hydrochloric | 20% | 25 | 3 | 0.007 |
| " | | " " | " | 50 | " | 0.028 |
| " | | " " | " | 75 | " | 0.038 |
| " | | " " | " | 100 | " | 0.120 |
| " | | " " | 10% | 25 | 2 | 0.0022 |
| " | | " " | " | 40 | " | 0.0039 |
| " | | " " | " | 50 | " | 0.0073 |
| " | | " " | " | 60 | " | 0.0108 |
| " | | " " | " | 70 | " | 0.0215 |
| " | | " " | " | 80 | " | 0.0286 |
| " | | " " | " | 90 | " | 0.0414 |
| " | | " " | " | 110 | " | 0.2050 |
| " | | " " | 5% | 25 | 3 | 0.001 |
| " | | " " | " | 50 | " | 0.002 |
| " | | " " | " | 75 | " | 0.004 |
| " | | " " | " | 100 | " | 0.003 |
| " | | " " | 1% | 25 | 3 | 0.001 |
| " | | " " | " | 50 | " | 0.002 |
| " | | " " | " | 5 | " | 0.004 |
| " | | " " | " | 100 | " | 0.003 |

| Metal | | Solution | | | | | Method No. | Rate of Corrosion Inches Penetration per Month |
|---|---|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | | | Temp. ° C. | | |
| Lead | | Acid sulphuric | 33.3% + sodium chloride | | 6.7% | 10 | 3 | 0.0001 |
| " | | " " | " " | " | " | 20 | " | 0.0007 |
| " | | " " | " " | " | " | 40 | " | 0.0008 |
| " | | " " | " " | " | " | 60 | " | 0.0007 |
| " | | " " | " " | " | " | 80 | " | 0.0032 |
| " | | " " | " " | " | " | 100 | " | 0.0148 |
| " | | " " | 31.0% + " | " | 17% | 5 | 3 | 0.0078 |
| " | | " " | " " | " | " | 0 | " | 0.0081 |
| " | | " " | " " | " | " | 50 | " | 0.0146 |
| " | | " " | " " | " | " | 75 | " | 0.0339 |
| " | | " " | " " | " | " | 100 | " | 0.0369 |
| " | | " " | 8.3% " | " | 1.7% | 20 | 3 | 0.0016 |
| " | | " " | " " | " | " | 40 | " | 0.0019 |
| " | | " " | " " | " | " | 60 | " | 0.0021 |
| " | | " " | " " | " | " | 80 | " | 0.0022 |
| " | | " " | " " | " | " | 100 | " | 0.0234 |
| Lead | | Caustic soda | 25% | | | 10 | 3 | 0.0004 |
| " | | " " | " | | | 20 | " | 0.0004 |
| " | | " " | " | | | 40 | " | 0.0002 |
| " | | " " | " | | | 60 | " | 0.0005 |
| " | | " " | " | | | 80 | " | 0.0007 |
| " | | " " | " | | | 100 | " | 0.0014 |
| Lead | | p-Nitro phenol | Saturated solution | | | 60 | 2 | 0.0012 |
| " | | " " | " | | | 40 | " | 0.0025 |
| " | | " " | " | | | 60 | " | 0.0038 |
| " | | " " | " | | | 100 | " | 0.0042 |
| Steel | Mild, hardness = 23 | Acid, hydrochloric | 10% | | | 40 | 2 | 0.0341 |
| " | do. | " " | " | | | 50 | " | 0.1005 |
| " | do. | " " | " | | | 60 | " | 0.2873 |
| " | do. | " " | " | | | 70 | " | 0.4060 |
| " | do. | " " | " | | | 80 | " | 0.9464 |

| Metal | Solution | Temp., ° C. | Rate of Corrosion. Inches Penetration per Month | Log Rate of Corrosion. Log Inches Penetration per Month |
|---|---|---|---|---|
| Aluminum[50]..... | Acid, Nitric, | 0 | 0.00024 | −3.62 |
| | Commercial, Sp. Gr. 1.42 | 8 | 0.00058 | −3.24 |
| | | 20 | 0.0021 | −2.68 |
| | | 30 | 0.0049 | −2.31 |
| | | 40 | 0.0091 | −2.04 |
| | | 50 | 0.0201 | −1.70 |
| | | 60 | 0.0411 | −1.39 |
| | | 70 | 0.0784 | −1.11 |
| | | 80 | 0.1528 | −0.82 |
| | | 90 | 0.2786 | −0.55 |
| | | 100 | 0.4765 | −0.32 |
| | | 110 | 0.7000 | −0.15 |
| | | 120 | 0.9300 | −0.03 |
| Lead..... | Acid Hydrochloric 10% | 25 | 0.0022 | −2.66 |
| | | 40 | 0.0039 | −2.41 |
| | | 50 | 0.0073 | −2.14 |
| | | 60 | 0.0108 | −1.97 |
| | | 70 | 0.0215 | −1.67 |
| | | 80 | 0.0286 | −1.54 |
| | | 90 | 0.0414 | −1.38 |
| | | 110 | 0.2050 | −0.69 |
| Steel, Mild..... | Acid, Hydrochloric 10% | 40 | 0.0341 | −1.47 |
| | | 50 | 0.1005 | −1.00 |
| | | 60 | 0.2837 | −2.55 |
| | | 70 | 0.4060 | −0.39 |
| | | 80 | 0.9464 | −0.02 |
| Iron, Cast..... | Acid, Hydrochloric 10% | 25 | 0.4381 | −0.36 |
| | | 40 | 0.6886 | −0.16 |
| | | 50 | 0.8089 | −0.09 |
| | | 60 | 1.0140 | 0.01 |
| | | 70 | 1.2615 | 0.10 |
| | | 80 | 1.5202 | 0.18 |
| | | 90 | 1.7606 | 0.25 |

*Calculations.*—

Representing data by straight line function,

$$\log C = \log A + BT$$

in which,

$C$ = rate of corrosion $\frac{(dw)}{(dt)}$

$T$ = temperature in °C

$\log A$ = the intercept on $\log C$ axis when $T = 0$

$B$ = slope of line

[50] Data calculated from Seligman and Williams, *J. Soc. Chem. Ind.*, *35*, 665 (1916)

*Aluminum in Nitric Acid:*

$$\log A = -3.22$$
$$\log C = -3.22 + BT$$

At $\log C = 0$, $\quad T = 109.5 \therefore B = \frac{3.22}{109.5} = 0.0294$

$$\log C = 0.0294T - 3.22$$

Rate of change of $C$ with temperature, $\frac{dC}{dT} = 0.0294C$

*Lead in Hydrochloric Acid:*

$$\log A = -3.25$$
$$\log C = -3.25 + BT$$

At $\log C = -1.00$, $\quad T = 103.5 \therefore B = \frac{2.25}{103.5} = 0.0217$

$$\log C = 0.0217T - 3.25$$

Rate of change of $C$ with temperature, $\frac{dC}{dT} = 0.0217C$

*Mild Steel in Hydrochloric Acid:*

$$\log A = -2.82$$
$$\log C = -2.82 + BT$$

At $\log C = 0$, $\quad T = 79.0 \therefore B = \frac{2.82}{79.0} = 0.0357$

$$\log C = 0.0357T - 2.82$$

Rate of change of $C$ with temperature, $\frac{dC}{dT} = 0.0357C$

*Cast Iron in Hydrochloric Acid:*

$$\log A = -0.51$$
$$\log C = -0.51 + BT$$

At $\log C = 0$, $\quad T = 60 \therefore B = \frac{0.51}{60} = 0.0085$

$$\log C = 0.0085T - 0.51$$

Rate of change of $C$ with temperature, $\frac{dC}{dT} = 0.0085$

TABLE V

EFFECT OF MISCELLANEOUS FACTORS IN LABORATORY TEST UPON RATE OF CORROSION RESULTS

*Shape of Test Piece:*

Metal: Lead. Pieces cast from same metal.
Solution: Hydrochloric Acid, 20 per cent, commercial.
Time of Exposure: 22.7 hrs.
Temperature of Solution: 25° C.

| Ratio $\frac{\text{Length of Edges (inches)}}{\text{Area (sq. in.)}}$ | Rate of Corrosion Inches Penetration per Month |
|---|---|
| 3.17 | 0.0058 |
| 3.88 | 0.0052 |
| 5.56 | 0.0055 |
| 8.52 | 0.0062 |

*Surface Finish of Test Piece:*

Metal: Cast Iron.
Solution: Sulphuric Acid, 90 per cent.
Time of Exposure: 64 hrs.
Temperature of Solution: 25°–30° C.
Average Rate of Corrosion (inches penetration per month):
Test Pieces Roughened on Coarse Grinding Wheel..... 0.00205
Test Pieces Polished by Metallographic Grinding..... 0.00265

Metal: Copper.
Solution: Acetic Acid, 83 per cent.
Method of Test: Standard (48–96 hr. measurement).
Temperature of Solution: 27° C. + 1° C.
Average Rate of Corrosion (inches penetration per month):
Test pieces roughened on coarse grinding wheel and then covered with file scratches..... 0.00015
Test pieces polished by metallographic grinding..... 0.00014

Metal: Aluminum.
Solution: Nitric Acid, 30 per cent., C. P.
Method of Test: Standard (48–96 hr. measurement).
Temperature of Solution: 27° C. + 1° C.
Average Rate of Corrosion (inches penetration per month):
Test pieces roughened on coarse grinding wheel and then covered with file scratches..... 0.0117
Test pieces polished by metallographic grinding..... 0.0113

*Volume of Corroding Solution:*

Metal: Lead.
Solution: Acetic Acid, 80 per cent.
Time of Exposure: 65.8 hrs.
Temperature of Solution: 25° C. ± 1°.
Average Rate of Corrosion (inches penetration per month):
100 cc. solution per test piece..... 0.0035
200 cc. solution per test piece..... 0.0065
400 cc. solution per test piece..... 0.0066

*Cleaning Test Pieces After Exposure:*

| Metal: | Mild Steel | Cast Iron | Lead | Lead |
|---|---|---|---|---|
| Method of Cleaning: (Cleaning methods indicated are several times as harsh as those ordinarily employed) | Scoured vigorously for ten minutes with "Old Dutch Cleanser" and piece of filter cloth. | | Boiled ten minutes in distilled water, finally wiped vigorously with cheese cloth. | Boiled ten minutes in 20% ammonium acetate solution, finally washed in distilled water and wiped vigorously with cheese cloth. |
| Average Rate of Corrosion (in/mo.) (based on 96 hr. exposure, error is zero if two measurements are made) . . . . | 0.00003 | 0.00004 | 0.00001 | 0.00002 |

## TABLE VI

### Effect of Velocity on Corrosion of Lead

| Solution | | | Velocity of Solution across Metal Surface ft./min. | Method No. | Rate of Corrosion. Inches Penetration per Month |
|---|---|---|---|---|---|
| Name | Description or Concentration | Temp. ° C. | | | |
| Acid | Hydrochloric 10% | 25 | 0.0 | 2 | 0.0052 |
| " | " " | " | 0.2 | " | 0.0137 |
| " | " " | " | 0.6 | " | 0.0194 |
| " | " " | " | 0.8 | " | 0.0191 |
| " | " " | " | 3.0 | " | 0.0239 |
| " | " " | " | 6.6 | " | 0.0215 |
| " | " " | " | 9.0 | " | 0.0257 |
| " | " " | " | 13 | " | 0.0255 |
| " | " " | " | 25 | " | 0.0308 |
| " | " 25% | " | 16 | 2 | 0.0256 |
| " | " " | " | 28 | " | 0.0300 |
| " | " " | " | 29 | " | 0.0311 |
| " | " " | " | 33 | " | 0.0399 |
| " | " 20% | " | 0.2 | 1 | 0.0187 |
| " | " " | " | 0.3 | " | 0.0280 |
| " | " " | " | 0.5 | " | 0.0240 |
| " | " " | " | 0.7 | " | 0.0257 |
| " | " " | " | 1.0 | " | 0.0335 |
| " | " " | " | 1.1 | " | 0.0252 |
| " | " " | " | 2.6 | " | 0.0204 |
| " | " " | " | 2.8 | " | 0.0237 |
| " | " " | " | 3.6 | " | 0.0197 |
| " | " " | " | 3.8 | " | 0.0238 |
| " | " " | " | 5.6 | " | 0.0254 |
| " | " " | " | 5.9 | " | 0.0288 |
| " | " " | " | 9.2 | " | 0.0325 |
| " | " " | " | 9.7 | " | 0.0351 |
| Acid | Sulphuric 20% | 25 | 8.4 | 2 | 0.00031 |
| " | " " | " | 13 | " | 0.00032 |
| " | " " | " | 18 | " | 0.00028 |
| " | " " | " | 35 | " | 0.00028 |
| " | " " | " | 8.4 | 2 | 0.00055 |
| " | " " | " | 11 | " | 0.00048 |
| " | " " | " | 16 | " | 0.00048 |
| " | " " | " | 17 | " | 0.00049 |
| " | " " | " | 97 | " | 0.00017 |
| " | " " | " | 155 | " | 0.00016 |
| " | " " | " | 300 | " | 0.00086 |
| " | " " | " | 260 | 3 | 0.0017 |
| " | " 9" | " | 290 | " | 0.0010 |
| " | " " | " | 320 | " | 0.0020 |
| " | " " | " | 350 | " | 0.0034 |
| " | " " | " | 280 | " | 0.00020 |
| " | " " | " | 190 | " | 0.00016 |
| Acid | Acetic Glacial | 25 | At rest | | 0.007 |
| " | " " | 25 | Impact | | 0.0458 |

## TABLE VII

### Measurements of Direct E.M.F. Between Metals

| Electrodes | | Solution | | Temp. ° C. | Electromotive Force, Millivolts |
|---|---|---|---|---|---|
| − | + | Name | Concentration | | |
| Iron, cast | Copper | Caustic, mixed | 25–50° Bé, KOH/NaOH = 10/7, some $CO_2$ | | 1.5–10.0 |
| | Steel, mild | Acid, sulphuric | 99% +5% Oleum (65%) | 25 | 3.5 |
| | | | | 95 | 50 |
| " " | " " | " " | 99% | 25 | 14.75 |
| " " | " " | Naph. sulf. mass | | 40 | 50 |
| " " | " " | " " " | | 25 | 1.5 |
| " " | " " | " " " | | 25 | 50 |
| " " | " C. R. | Acid, sulphuric | 60% | 50 | 19 |
| " " | " Rivet | " " | " | 50 | 21 |
| " " | " Pipe No. 1 | " " | " | 50 | 50 |
| Steel, rivet | Pipe (No. 1) | " " | " | 50 | 27 |
| " " | Boiler plate No. 1 | " " | " | 50 | 30 |
| " " | " " No. 2 | " " | " | 50 | 1 |
| " C. R. | Pipe No. 1 | " " | " | 50 | 15 |
| " C. R. | Steel rivet | " " | " | 50 | 10 |
| " C. R. | " boiler plate (No. 2) | " " | " | 50 | 10 |
| " boiler plate (No. 1) | Pipe (No. 1) | " " | " | 50 | 50 |
| " " " (No. 1) | " (No. 2) | " " | " | 50 | 36 |
| " " " (No. 1) | " (No. 3) | " " | " | 50 | 39 |
| " " " (No. 1) | Steel rivet | " " | " | 50 | 1 |
| " boiler plate (No. 2) | Pipe (No. 2) | " " | " | 50 | 20 |
| " " " (No. 2) | " (No. 3) | " " | " | 50 | 30 |
| Pipe No. 1 | Steel boiler plate (No. 2) | " " | " | 50 | 33 |
| Pipe (Hydr.) | " " " (No. 1) | " " | " | 50 | 32.5 |
| " " | " " " (No. 2) | " " | " | 50 | 50 |
| Brass (No. 2) | " " " (No. 1) | " " | " | 50 | 7 |
| " " | " " " (No. 2) | " " | " | 50 | 6 |
| " " | " " " | " " | " | 50 | 5 |
| Iron | Charcoal steel | Caustic, mixed | 25–50° Bé, KOH/NaOH = 10/7, some $CO_2$ | 25 | 0.3 |
| " | " " | " " | do. | 115 | 1.0 |
| Steel | " " | " " | do. | 25 | 0.0 |
| " | " " | " " | do. | 115 | 0.5 |

## TABLE VIII

### Corrosion of Metals by Solutions at Rest

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| Alloy | Spec. Lumen Bearing Co. | Acid | 1.55% calc. as $H_2SO_4$. Wood digestion in alcohol plant | 80 | 3 | 0.00028 |
| " | Ceco, Al +small % rare earths | " acetic | 20% | 25 | 1 | 0.0022 |
| | | | 20 | B.P. | | 0.0190 |
| | | | 60 | 25 | | 0.0019 |
| | | | 60 | B.P. | | 0.0180 |
| | | | 100 | 25 | | 0.00011 |
| | | | 100 | B.P. | | 0.00039 |
| | | | *Acid Anhydride* | | | |
| " | " " " | " " +acetic anhyd. | 90% 10% | 25 | 1 | 0.000493 |
| | | | 90 10 | B.P. | | 0.235 |
| | | | 40 60 | 25 | | 0.000214 |
| | | | 40 60 | B.P. | | 0.220 |
| | | | 20 80 | 25 | | 0.000087 |
| | | | 20 80 | B.P. | | 0.0181 |
| " | " " " | Acid, nitric | 5% | 25 | 1 | 0.0205 |
| | | | 5 | 50 | | 0.0562 |
| | | | 50 | 25 | | 0.0731 |
| | | | 50 | 50 | | 1.130 |
| | | | 63 (comm.) | 25 | | 0.0655 |
| | | | 63 (C.P.) | 25 | | 0.0918 |
| | | | 63 (comm.) | 50 | | 0.230 |
| | | | 63 (C.P.) | 50 | | 0.288 |
| | | | 95 | 25 | | 0.00072 |
| | | | 95 | 50 | | 0.00340 |

TABLE VIII—*Continued*

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| Alloy | Ulcaloy (United Lead Co.) | | | | | |
| | No. 1 Pb–Cu | Acid, nitric | 90% | 25 | 3 | 0.15 |
| | | | 90 | 70–80 | | 0.78 |
| | No. 2 Pb–Cu | " " | 50 | 25 | | 15.16 |
| | No. 1 Pb–Cu | " sulphuric | 5 | 25 | | 0.002 |
| | | | 5 | 70–80 | | 0.006 |
| | No. 2 Pb–Cu | " " | 5 | 25 | | 0.0000 |
| | | | 5 | 70–80 | | 0.006 |
| | No. 3 Pb–Cu | " " | 5 | 25 | | 0.000 |
| | | | 5 | 70–80 | | 0.000 |
| Aluminum | | " acetic | 20 | 25 | 1 | 0.000034 |
| | | | 20 | B.P. | | 0.0185 |
| | | | 60 | 25 | | 0.000033 |
| | | | 60 | B.P. | | 0.0183 |
| | | | 100 | 25 | | 0.000008 |
| | | | 100 | B.P. | | 0.000019 |
| | Pure sheet | " " | 20 | 25 | | 0.0030 |
| | | | 20 | B.P. | | 0.0230 |
| | | | 60 | 25 | | 0.0021 |
| | | | 60 | B.P. | | 0.0170 |
| | | | 100 | 25 | | 0.056 |
| | | | 100 | B.P. | | 0.000014 |
| " | | Acetic anhydride | C.P. | 25 | 1 | 0.00002 |
| | | " " | C.P. | 60 | | 0.00043 |

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| Aluminum | | Acid, mixed | 40% $H_2SO_4$, 60% $HNO_3$ | 20 | 3 | 0.0075 |
| | | | 30 70 | | | 0.0068 |
| | | | 20 80 | | | 0.0051 |
| | | | 10 90 | | | 0.0033 |
| | | | 0 100 | | | 0.0007 |
| | | | 100 0 | | | 0.0054 |
| | | | 90 10 | | | 0.0077 |
| | | | 80 20 | | | 0.0078 |
| | | | 70 30 | | | 0.0079 |
| | | | 60 40 | | | 0.0079 |
| | | | 50 50 | | | 0.0078 |
| | | " nitric | 30% (roughened) | 27 | 1 | 0.0117 |
| | | | (polished) | | | 0.0113 |
| " | Unannealed sheet | " " | C.P. 70% | | 3 | 0.0031 |
| | | | 60 | | | 0.0052 |
| | | | 50 | | | 0.0080 |
| | | | 40 | | | 0.0087 |
| " | " " | " " | 69.6% | 20 | | 0.00133 |
| | | | 89.0 | | | 0.00044 |
| | | | 90.8 | | | 0.00013 |
| | | | 96.1 | | | 0.0002 |
| | | | 99.5 | | | 0.000005 |
| " | " " | " sulphuric | 5% | 25 | (25 hr.) | 0.007 |
| | | | 10 | | | 0.013 |
| | | | 20 | | | 0.010 |

TABLE VIII—*Continued*

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| | | | 30% | | | 0.017 |
| | | | 40 | | | 0.020 |
| | | | 40 | | | 0.020 |
| | | | 50 | | | 0.039 |
| Aterite | Cu 60.6, Ni 10.8, Zn 27.3, Sb 0.4, undetermined 0.9 | " acetic | Glacial | 31 | 3 | 0.0004 |
| | | " sulphuric | 75% | B.P. | 3 | 0.02 |
| | | | | 100 | | 0.0004 |
| | | | | 70 | | 0.0001 |
| | | | | 31 | | 0.0004 |
| Bakelite | Dilecto | " acetic | 99% | 25 | 1 | 0.0031 |
| | | " hydrochloric | 30 | 100 | 1 | 0.0903 |
| | | " nitric | 68 | 25 | 1 | 0.0896 |
| | | Oil | Lubricating | 130 | 1 | 0.034 |
| Brass | Cast rough | Acid, mixed | 98% $H_2SO_4$, 2% $HNO_3$ | 50 | 3 | 0.0089 |
| " | " " | " 1.55% calc. as sulphuric—Wood digestion in alcohol plant | | 80 | 3 | 0.00028 |
| " | Sheet | Alum solution | 38° Bé | 100 | 1 | 0.00721 |
| Brick | Chemical ware | Sodium hydroxide | 30% | 90 | 1 | 0.195 |
| | | " sulphide | | 90 | | 0.072 |
| | | Above mixed | NaOH 15%, $Na_2S$ 15% | 90 | | 0.094 |
| Bronze | BB | Acid, 1.55% calc. as sulphuric—Wood digestion in alcohol plant | | 80 | 3 | 0.00074 |
| " | Cramp's | do. | | | | 0.00012 |
| " | Lead | do. | | | | 0.00034 |

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| Bronze | Manganese | do. | | | | 0.00016 |
| " | " Parson's | do. | | | | 0.00012 |
| " | Phospher | do. | | | | 0.00021 |
| " | Tin | do. | | | | 0.00023 |
| " | Zinc-lead | do. | | | | 0.00026 |
| " | Tobin | Alum solution | 38° Bé | 100 | 1 | 0.00726 |
| Cement | Positive seal | Acid, acetic | 80% | | 1 | 0.001213 |
| | | | 99+ | | | 0.00391 |
| | | | 80 | | | 0.00054 |
| | | | 99+ | | | 0.003067 |
| Copper | | Acetic anhydride | | 75 | 3 | 0.0040 |
| | | | | 25 | | 0.0002 |
| " | | Acid, acetic | 32.96% | 100 | 3 | 0.00172 |
| | | | 68.21 | 105 | | 0.001623 |
| | | | 83.25 | 110 | | 0.000032 |
| | | | 95.54 | 115 | | 0.000254 |
| | | | 97.85 | 119 | | 0.000223 |
| | | | 20 | 25 | 1 | 0.000128 |
| | | | 20 | B.P. | | 0.00555 |
| | | | 60 | 25 | | 0.00047 |
| | | | 60 | B.P. | | 0.00101 |
| | | | 100 | 25 | | 0.00069 |
| | | | 100 | B.P. | | 0.0229 |
| | | | 83 (roughened) | 27 | | 0.00015 |
| | | | 83 (polished) | 27 | | 0.00014 |
| | | | Glacial | 25 | 3 | 0.0015 |
| | | | " | 50 | | 0.0550 |
| | | " " plus acetic anhydride | 20% acid, 80% anhyd. | 25 | 1 | 0.000148 |

TABLE VIII—*Continued*

| Metal | | Solution | | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | | Temp. ° C. | Method No. | Inches Penetration per Month |
| | | | 20% | 80% | B.P. | | 0.0269 |
| | | | 20 | 80 | 100 | | 0.0095 |
| | | | 20 | 80 (air pres.) | 100 | | 0.0660 |
| | | | 40 | 60 | 50 | | 0.00422 |
| | | | 40 | 60 (air pres.) | 50 | | 0.00355 |
| | | | 90 | 10 | 25 | | 0.00050 |
| | | | 90 | 10 | B.P. | | 0.0414 |
| | | | 40 | 60 | 25 | | 0.000079 |
| | | | 40 | 60 | B.P. | | 0.0393 |
| Copper | | Acid, chloracetic | Sp. Gr. 1.358 at 50° C. | | 100 | 1 | 0.0218 |
| " | | " hydrochloric | 1.8% | | 25 | 1 | 0.00928 |
| | | | 35.5 | | B.P. | | 0.0903 |
| " | | " nitric | 3 | | 25 | 1 | 0.00161 |
| " | Very pure | " 1.55% calc. as sulphuric—Wood digestion in alcohol plant | | | 80 | 1 | 0.0005 |
| " | | Caustic $\frac{KOH}{NaOH} = \frac{10}{7}$ | 25–50° Bé | | B.P. | 3 | 0.0016 |
| " | | Rongalite solution | 90% | | 75 | 2 | 0.00047 |
| | | | | | | | 0.00035 |
| Iron | Cast | Acid, acetic | 20% | | 25 | 1 | 0.0591 |
| | | | | | B.P. | | 0.213 |
| | | | 60 | | 25 | | 0.746 |
| | | | | | B.P. | | 0.956 |
| | | | 100 | | 25 | | 0.0032 |
| | | | | | B.P. | | 0.0192 |
| | | | 20 (0.7% $As_2O_3$) | | 25 | | 0.0036 |
| | | " " plus acetic anhydride | 20% acid, 80% anhyd. | | 25 | 1 | 0.00219 |
| | | | | | B.P. | | 0.0121 |
| | | | 40 | 60 | 25 | | 0.00161 |
| | | | | | B.P. | | 0.0502 |
| | | | 90 | 10 | 25 | | 0.0049 |

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| Iron | | | | B.P. | | 0.113 |
| " | " Soft H =8 | Acid, chloracetic | Sp. Gr. 1.358 at 50° C. | | 1 | 0.0238 |
| " | " " " | " hydrochloric | 10% | 20–30 | 3 | 0.256 |
| | | | | 80–88 | | Very high |
| | | | 27 | 20–30 | | 0.36 |
| | | | | 80–88 | | Very high |
| | | | 10 (0.7% $As_2O_3$) | 250 | | 0.00026 |
| " | " " " | " mixed | 60% $H_2SO_4$, 23.5% $HNO_3$ | 25 | 1 | 0.00272 |
| | | | | | | 0.00170 |
| | | | 60 23.5 | 25 | | 0.00241 |
| | | | (Contact with mild steel) | | | 0.00153 |
| " | " " " | " nitric | 10% | 20–30 | 3 | 0.315 |
| | | | | 80–88 | | 0.611 |
| | | | 85–90 | 20–30 | | 0.0345 |
| | | | | 80–88 | | 0.49 |
| " | " " " | " sulphuric | 10 | 20–30 | 3 | 0.197 |
| | | | | 80–88 | | 0.248 |
| | | | 93 | 20–30 | | 0.001 |
| | | | | 80–88 | | 0.019 |
| | | | 99 | 40 | | 0.010 |
| | | | Oleum | 20–30 | | 0.0013 |
| | | | | 80–88 | | 0.0139 |
| | | | 93 | 25 (30-day test) | | 0.0015 |
| | | | 10 (0.7% $As_2O_3$) | 25 | 1 | 0.0786 |
| | | | 1.55 (roughened) | 80 | 3 | 0.0423 |
| | | | (polished) | | | 0.0492 |
| " | " " " | Antimony pentachloride | 100 | 100 | 1 | 0.0081 |
| " | " " " | " trichloride | 100 | 100 | 1 | 0.00071 |

TABLE VIII—*Continued*

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| Iron | Cast, H = 8 | Caustic, mixed, $\frac{KOH}{NaOH} = \frac{10}{7}$ | 25–50° Bé | B.P. | 3 | 0.0491 |
| | | | 40–50° Bé | B.P. | 3 | 0.0025 |
| | | | 25–50° Bé | B.P. | 2 | 0.0295 |
| | | p-Nitraniline $\frac{PNA}{NH_3(28\%)} = \frac{1}{4.66}$ | | 160 | 3 | Unaffected |
| | | Nitrobenzene $\frac{NB}{(87\%)HNO_3} = \frac{8}{1}$ | | 55 | 1 | 0.0508 |
| | | m-Nitrochlorbenzol, dehydrated | | | 2 | 0.0009 |
| | | Sodium hydrosulphite | 20%, Comm. (95%) | 25 | 2 (30-day test) | 0.0081 |
| Wrought Corrosiron | No. 42 | Caustic soda | 50–40° Bé | B.P. | 2 | 0.0025 |
| | | Acid, hydrochloric | 10% | 20–30 | 3 | 9.0015 |
| | | | | 80–88 | | 0.0167 |
| | | | 27 | 20–30 | | 0.0248 |
| | | | | 80–88 | | 0.154 |
| " | No. 42 | Acid, nitric | 10% | 20–30 | 3 | 0.0004 |
| | | | | 80–88 | | 0.002 |
| | | | 85-90% | 20–30 | | 0.00006 |
| | | | | 80–88 | | 0.0004 |
| " | No. 42 | " sulphuric | 10% | 20–30 | | 0.0234 |
| | | | | 80–88 | | 0.0230 |
| | | | 93% | 20–30 | | 0.0001 |
| | | | | 80–88 | | 0.0001 |

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| | | | Oleum | 20–30 | | 0.003 |
| | | | | 80–88 | | 0.085 |
| | Wrought Corrosiron No. 148 | " hydrochloric | 10% | 20–30 | 3 | 0.001 |
| | | | | 80–88 | | 0.018 |
| | | | 27 | 20–30 | | 0.0075 |
| | | | | 80–88 | | 9.124 |
| | | " nitric | 10% | 20–30 | 3 | 0.0000 |
| | | | | 80–88 | | 0.0001 |
| | | | 85–90 | 20–30 | | 0.0000 |
| | | | | 80–88 | | 0.0000 |
| Iron | Corrosiron No. 148 | Acid, sulphuric | 10% | 20–30 | 3 | 0.0007 |
| | | | | 80–88 | | 0.0072 |
| | | | 93 | 20–30 | | 0.0000 |
| | | | | 80–88 | | 0.0002 |
| | | " " | Oleum | 20–30 | | 0.0156 |
| | | | | 80–88 | | 0.121 |
| | " No. 152 | " hydrochloric | 10% | 20–30 | 3 | 0.001 |
| | | | | 80–88 | | 0.014 |
| | | | 27 | 20–30 | 3 | 0.0059 |
| | | | | 80–88 | | 0.193 |
| | | " nitric | 10% | 20–30 | 3 | 0.0004 |
| | | | | 80–88 | | 0.0016 |
| | | | 85–90 | 20–30 | | 0.0000 |
| | | | | 80–88 | | 0.0001 |
| | | " sulphuric | 10 | 20–30 | 3 | 0.001 |
| | | | | 80–88 | | 0.007 |
| | | | 93 | 20–30 | | 0.0000 |
| | | | | 80–88 | | 0.0004 |
| | | | Oleum | 20–30 | | 0.0141 |
| | | | | 80–88 | | 0.0895 |

TABLE VIII—*Continued*

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| Iron | Duriron | Acid, acetic | 20% | 25 | 1 | 0.00646 |
| | | | | B.P. | | 0.00779 |
| | | | 60 | 25 | | 0.00066 |
| | | | | B.P. | | 0.00121 |
| | | | 100 | 25 | | 0.000105 |
| | | | | B.P. | | 0.000985 |
| | | | 99.49 (NaCl present) | 98 | 3 | 0.00040 |
| | Duriron | Acetic anhydride | C.P. | 60 | 1 | 0.000095 |
| | Duriron | Acid, acetic | 99 | 25 | 1 | 0.00012 |
| | | | | 60 | | 0.00019 |
| | | | 99.5 | 25 | | 0.00012 |
| | | | | 60 | | 0.00019 |
| | | " + anhydride | Anhy. Acid | | | |
| | | | 10% 90% | 25 | 1 | 0.000055 |
| | | | 10 90 | B.P. | | 0.000107 |
| | | | 60 40 | 25 | | 0.00040 |
| | | | 60 40 | B.P. | | 0.00095 |
| | | | 80 20 | 25 | | 0.00013 |
| | | | 80 20 | B.P. | | 0.0051 |
| | | " hydrochloric | 10% | 24 | | 0.00163 |
| | | | 10 | 43 | | 0.00503 |
| | | | 36.21 | 24 | | 0.00424 |
| | | | 36.21 | 85 | | 0.19000 |
| | | " sulphuric | 25 | 25 | 3 | 0.00001 |
| | | | 25 | 80 | | 0.00023 |
| | | | 2 | 140° F. | (Loss in 72 hrs.) | 0.01 |
| | | | 5 | 140° F. | (Loss in 72 hrs.) | 0.01 |
| | Tantiron | Acid, hydrochloric | 2 | 25 | 1 | 0.00081 |
| | | | 20 | 25 | 1 | 0.00063 |

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| | | | 2% | 60 | | 0.00265 |
| | | | 20 | 60 | | 0.01150 |
| | | " nitric | 10 | 25 | 1 | 0.01180 |
| | | | 70 | 25 | | 0.00078 |
| | | | 10 | 60 | | 0.01560 |
| | | | 70 | 60 | | 0.00252 |
| | | " sulphuric | 1 | 25 | 1 | 0.00061 |
| | | | 10 | | | 0.00668 |
| | | | 20 | | | 0.00012 |
| | | | 50 | | | 0.00081 |
| | | | 100 | | | 0.00074 |
| | | | 1 | 60 | | 0.00181 |
| | | | 10 | | | 0.00802 |
| | | | 20 | | | 0.00152 |
| | | | 50 | | | 0.00234 |
| | | | 100 | | | 0.00076 |
| Lead | | Acid, acetic | 4 | Room | 1 | 0.00177 |
| | | | 3 | | | 0.00175 |
| | | | 2 | | | 0.00183 |
| | | | 1 | | | 0.00162 |
| | | | 0.5 | | | 0.00162 |
| | | | 5 | | | 0.0024 |
| | | | 10 | | | 0.0015 |
| | | | 20 | | | 0.0023 |
| | | | 40 | | | 0.0018 |
| | | | 60 | | | 0.0023 |
| | | | Glacial 98% | 25 | 2 | 0.007 |
| | | | | 50 | | 0.020 |
| | | " | 99.5+5% $S_2Cl_2$ | 25 | | 0.0002 |
| | | | | 50 | | 0.001 |
| | | | | 75 | | 0.021 |
| | | | | 70 | 3 | 0.0006 |

TABLE VIII—*Continued*

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| Lead | | Glacial saturated with lead acetate | | 70 | 1 | 0.0024 |
| | | Acetic, | 79.9% | 25 | | 0.0066 |
| | | Glacial saturated with sodium sulphate | | 25 | | 0.0044 |
| | | Acid, Chloracetic, | sp. gr. 1.358 at 50° C. | | | |
| | | | | 10 | | 0.0547 |
| | | Acid, Hydrochloric | 1% | 25 | 3 | 0.001 |
| | | | | 100 | | 0.003 |
| | | | 5 | 25 | | 0.0015 |
| | | | | 100 | | 0.0045 |
| | | | 10 | 25 | | 0.001 |
| | | | | 100 | | 0.013 |
| | | | 20 | 25 | | 0.007 |
| | | | | 100 | | 0.120 |
| | | | comm'l 20% | 25 | 2 | 0.0055 |
| | | | 35.5 | 25 | | 0.091 |
| | | | | 100 | | 0.172 |
| | | | 10 | 70 | 3 | 0.0138 |
| | | | 10% sat'd with $PbCl_2$ | 70 | | 0.0105 |
| | | | Nitric 2% | 70 | 2 | 0.2034 |
| | | | 2% + sat'd sol'n lead nitrate | 70 | | 0.4299 |
| Lead | | Acid, nitric | 10% | 25 | (6 test hrs.) | 0.609 |
| " | | " " plus $Na_2SO_4.10\ H_2O$ | 4.0% $HNO_3$, 0% $Na_2SO_4$ | 55 | 1 | 0.121 |
| | | | 1.0 | | | 0.108 |
| | | | 5.0 | | | 0.111 |
| | | | 10.0 | | | 0.00365 |
| | | | 20.0 | | | 0.00049 |
| | | | 30.0 | | | 0.00029 |

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| Lead | | Acid, sulphuric | 2.4% | 25 | 1 | 0.000165 |
| | | | 5 | | | 0.000024 |
| " | | " " | 105% | 40 | 3 | 0.41 |
| | | | | 70 | | 0.95 |
| " | | " " +HCl | 20% $H_2SO_4$, 0% HCl | 25 | 2 | 0.0001 |
| | | | 18 2 | | | 0.0032 |
| | | | 15 5 | | | 0.0179 |
| | | | 10 10 | | | 0.0489 |
| | | | 5 15 | | | 0.0856 |
| | | | 2 18 | | | 0.1326 |
| | | Mixed acid | 18 2% $HNO_3$ | | | 0.2478 |
| | | | 15 5 | | | Very great |
| | | | 10 10 | | | " " |
| | | | 5 15 | | | " " |
| | | | 2 18 | | | " " |
| " | | Acid, sulphuric + NaCl | 8.3 1.7 NaCl | 20 | 3 | 0.0016 |
| | | | | 100 | | 0.0234 |
| | | | 16.7 3.3 | 20 | | 0.0002 |
| | | | | 100 | | 0.0265 |
| | | | 31.0 17.0 | 30 | | 0.0081 |
| | | | | 100 | | 0.0369 |
| | | | 33.3 6.7 | 20 | | 0.0007 |
| | | | | 100 | | 0.0148 |
| | | | 50.0 10 | 20 | | 0.0010 |
| | | | | 100 | | 0.0034 |
| " | | " $H_2SO_4$ 39.8%, $H_2O$ 27.6%, R-salt 17.8%, Michler's hydrol 14.8% | | 100 | 1 | 0.0026 |
| " | | Caustic soda | 5% | 20 | 3 | 0.0011 |
| | | | | 100 | | 0.0035 |

TABLE VIII—*Continued*

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| | | Caustic soda | 15% | 20 | 2 | 0.0004 |
| | | | | 40 | | 0.0002 |
| | | | | 60 | | 0.0005 |
| | | | | 80 | | 0.0007 |
| | | | | 100 | | 0.0014 |
| | | | 25 | 20 | 3 | 0.0004 |
| | | | | 100 | | 0.0010 |
| | | | 35 | 20 | | 0.0003 |
| | | | | 100 | | 0.0005 |
| Lead | | Lead acetate, p-nitrophenol | Saturated solution | 70 | 2 | 0.0783 |
| | | | " | 40 | | 0.0025 |
| | | | | 100 | | 0.0042 |
| | | Sodium hydrosulphite, | 20% comm. (95%) | 25 | 3 | 0.00007 |
| | | Sodium sulfide | 5% | 25 | | 0.002 |
| | | | | 100 | | 0.001 |
| | | | 10 | 25 | | 0.001 |
| | | | | 100 | | 0.001 |
| | | | 15 | 25 | | 0.001 |
| | | | | 100 | | 0.001 |
| | | | 20 | 25 | | 0.001 |
| | | | | 100 | | 0.001 |
| | | | 25 | 25 | | 0.001 |
| | | | | 100 | | 0.001 |
| | | Alum solution | 38° Bé | 100 | 1 | 0.00174 |
| | | Antimony trichloride | 100% | 100 | 1 | 0.0049 |
| Lead—hard (Sb) | | Acid, hydrochloric | 1 | 20 | 3 | 0.0001 |

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| Lead, hard | | | | 100 | | 0.0001 |
| | | | 5% | 20 | | 0.0001 |
| | | | | 100 | | 0.0006 |
| | | | 10 | 20 | | 0.0002 |
| | | | | 100 | | 0.0006 |
| | | | 35 | 20 | | 0.0010 |
| | | | | 100 | | 0.0024 |
| | | Acid, sulphuric | 1 | 20 | | 0.00002 |
| | | | | 100 | | 0.00006 |
| | | | 10 | 20 | 3 | 0.00006 |
| | | | | 100 | | 0.00003 |
| | | | 50 | 20 | | 0.00001 |
| | | | | 100 | | 0.0002 |
| | | | 95 | 20 | | 0.0001 |
| | | | | 100 | | 0.0041 |
| " -tin solder | | Rongalite sol'n | 40 | 95–100 | 2 | 0.0005 |
| | | | 90 | | | 0.000185 |
| | | Polysulfide sol'n | $Na_2S$ 8.3%, S 6.0% | B.P. | 1 | 1.15 |
| Meco metal | 50% Pb, 50% Cu | Acid, HCl | 20% | 25 | 1 | 0.00140 |
| | | | 20 | 60 | | 0.03040 |
| | | | 2 | 25 | | 0.00020 |
| | | | 2 | 60 | | 0.00153 |
| | | " $H_2SO_4$ | 1 | 45 | 1 | 0.00038 |
| | | | 10 | | | 0.00028 |
| | | | 20 | | | 0.00023 |
| | | | 50 | | | 0.00016 |
| | | | 100 | | | 0.00291 |
| | | | 1 | 30 | | 0.00015 |
| | | | 10 | | | 0.00016 |

TABLE VIII—*Continued*

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| | | | 20% | | | 0.00013 |
| | | | 50 | | | 0.00004 |
| | | | 100 | | | 0.00186 |
| Monel metal | | Acid, acetic | 99 | 25 | | 0.00016 |
| | | | | 60 | | 0.0024 |
| | | | | 100 | | 0.040 |
| | | " H- | Disodium salt 20% sol'n | 25 | | 0.00007 |
| | | | | 60 | | 0.00012 |
| | | | | 100 | | 0.00015 |
| | | " HCl | 10% | 60 | | 0.0071 |
| | | | | 80 | | 0.024 |
| | | | 20 | 25 | | 0.0008 |
| | | | | 60 | | 0.054 |
| | | | | 80 | | 0.228 |
| | | " mixed | $H_2SO_4$ 52.80, $HNO_3$ 45.65 $HNOSO_4$ 1.28, $H_2O$ 0.27 | 35 | | 0.00070 |
| | | | | | | 0.00072 |
| Monel metal | | Acid, nitric | 30 | 25 | 1 | Diss. readily |
| | | | 76 | | | " " |
| | | " $H_2SO_4$ | 10 | 80 | | 0.00054 |
| | | | | 100 | | 0.00059 |
| | | | 50 | 25 | | 0.00021 |
| | | | | 60 | | 0.00135 |
| | | | 1 | 25 | | 0.00009 |
| | | | | 60 | | 0.00076 |
| | | | | 100 | | 0.0035 |
| | | | 10 | 25 | | 0.00025 |
| | | | | 60 | | 0.00043 |
| | | 1.55% calc. as $H_2SO_4$. Wood digestion in alcohol plant | | 80 | 3 | 0.00020 |

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| | | Alum sol'n | 38° Bé | 100 | 1 | 0.00517 |
| | | Caustic soda | 20% | 100 | 1 | 0.000004 |
| | | Sodium chloride | 10 | 100 | | 0.00043 |
| | | " hydrosulphite | $Na_2S_2O_4$ 10, NaOH 1 | 80 | | 0.00017 |
| Nickel | | Acid, chloracetic | Sp. Gr. 1.358 at 50° | 100 | 1 | 0.0019 |
| | | " hydrochloric | 15% | 25 | 1 | 0.0023 |
| | | | | 200 | | Diss. readily |
| Pyralin | | Acid, acetic | 10 | 25 | 1 | 0.006 |
| | | | 99 | | | Diss. readily |
| | | " hydrochloric | 10 | | | 0.0035 |
| | | | 37 | | | 0.063 |
| | | " mixed sulphuric and nitric | $H_2SO_4$ $HNO_3$ | | | |
| | | | 15% 5% | 25 | 1 | 0.0043 |
| | | | 10 10 | | | 0.055 |
| | | | 5 15 | | | 0.0028 |
| | | | 65 32 | | | Diss. slowly |
| | | | 42 54 | | | " " |
| | | | 20 73 | | | " " |
| | | " nitric | 10% | 25 | 1 | 0.0024 |
| | | | 40 | | | 0.0035 |
| | | " sulphuric | 10 | 25 | 1 | 0.148 |
| | | | 50 | | | 0.0046 |
| | | | 77 | | | 0.097 |
| | | | 93 | | | Diss. readily |
| | | Caustic soda | 10 | 25 | 1 | 0.033 |
| | | | 25 | | | 0.292 |
| | | | 40 | | | 0.141 |
| Silver | Coin | Acid hydrochloric | 15 | 25 | 1 | 0.00104 |
| | | | 15 | 150 | 1 | destroyed |

TABLE VIII—*Continued*

| Metal | | Solution | | Rate of Corrosion | | |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| Steel | Mild | Acid, mixed | $H_2SO_4$ 60%, $HNO_3$ 23.5% | 25 | 1 | 0.00104 |
| | | " " | " 72.5 " 27 | 25 | | 0.00140 |
| | | | " 52.8 " 45.65 | 35 | 1 | 0.000255 |
| | | | $HNOSO_4$ 1.28 $H_2O$ 0.27 | | | |
| | | Antimony pentachloride | 100% | 100 | 1 | 0.0118 |
| | | " trichloride | 100 | 100 | 1 | 0.00030 |
| | | Sodium bisulphite | 20 | 25 | 1 | 0.00135 |
| " | Medium (tank) | Acid, hydrochloric | 10 | 20–30 | 3 | 0.044 |
| " | " " | " " | | 80–88 | | Very high |
| " | " (bar) | " " | 10 | 20–30 | | 0.435 |
| " | " " | " " | | 80–88 | | Very high |
| " | " (tank) | " " | 27 | 20–30 | | 0.41 |
| " | " " | " " | | 80–88 | | Very high |
| " | " (bar) | " " | 27 | 20–30 | | 0.26 |
| " | " " | " " | | 80–88 | | Very high |
| " | " (tank) | " nitric | 10 | 20–30 | 3 | 0.614 |
| " | " " | " " | | 80–88 | | 1.175 |
| " | " (bar) | " " | 10 | 20–30 | | 0.414 |
| " | " " | " " | | 80–88 | | 0.741 |
| " | " (tank) | " " | 85–90 | 20–30 | | 0.128 |
| " | " " | " " | | 80–88 | | 0.57 |
| " | " (bar) | " " | 85–90 | 20–30 | | 0.009 |
| " | " " | " " | | 80–88 | | 0.29 |
| " | " (tank) | " sulphuric | 10 | 20–30 | 3 | 0.49 |
| " | " " | " " | | 80–88 | | 0.45 |
| " | " (bar) | " " | 10 | 20–30 | | 0.25 |
| " | " " | " " | | 80–88 | | 0.325 |

| Metal | | Solution | | | Laboratory Work | Rate of Corrosion |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| Steel | Medium (tank) | Acid sulphuric | 93% | 20-30 | | 0.0017 |
| " | " " | " " | | 80-88 | | 0.0194 |
| " | " (bar) | " " | 93 | 20-30 | | 0.0019 |
| " | " " | " " | | 80-88 | | 0.0123 |
| " | " " | " " | Oleum | 20-30 | 3 | 0.0019 |
| " | " " | " " | " | 80-88 | | 0.0016 |
| " | " (tank) | " " | " | 20-30 | | 0.0015 |
| " | " " | " " | " | 80-88 | | 0.0015 |
| " | Mild | " , mixed aliphatic, 1.55% calc. as $H_2SO_4$ | | 80 | 3 | 0.0067 |
| " | " H =23 | " acetic | 97% | 25 | 3 | 0.0049 |
| " | " | " " | 97 | 75 | | 0.145 |
| " | " | " " | 97.5 | 25 | | 0.0044 |
| " | " | " " | 98.0 | 25 | | 0.0051 |
| " | " | " " | 98.0 | 75 | | 0.177 |
| " | " | " " | 98.5 | 25 | | 0.0057 |
| " | " | " " | 99.0 | 25 | | 0.0056 |
| " | " | " " | 99.0 | 40 | | 0.025 |
| " | " | Sodium hydrosulphite | 20% comm. (95% $Na_2S_2O_4$) | 25 | 2 | 0.0044 |
| " | " | Sodium hypochlorite | | 25 | 2 | 0.00003 |
| " | " | Water, river, Delaware | | | 2 | 0.0100 |

TABLE VIII—*Continued*

| Metal | | Solution | | | Laboratory Work | Rate of Corrosion |
|---|---|---|---|---|---|---|
| Name | Description | Name | Description or Concentration | Temp. ° C. | Method No. | Inches Penetration per Month |
| Tin | Block | Acid, acetic | 20% | 25 | 1 | 0.000412 |
| | | | | B.P. | | 0.000896 |
| | | | 60 | 25 | | 0.000511 |
| | | | | B.P. | | 0.00131 |
| | | | 100 | 25 | | 0.00160 |
| | | | | | | 0.0140 |
| | | " " +anhydride | Acid Anhy. | | | |
| | | | 10% 90% | 25 | | 0.00169 |
| | | | | B.P. | | 0.0103 |
| | | | 60 40 | 25 | | 0.00140 |
| | | | | B.P. | | 0.0456 |
| | | | 80 20 | 25 | | 0.00405 |
| | | | | B.P. | | 0.0588 |
| Zinc | Galvanized iron | Polysulfide sol. | $Na_2S$ 8.3%, S 6.0% | B.P. | 1 | 0.0012 |
| | | Rongalite sol'n | 40% | 95–100 | 2 | 0.0077 |
| | | | 40 | | | 0.0032 |
| | | | 90 | 75 | | 0.00784 |
| | | | 90 | | | 0.00775 |

## SUMMARY

| Solution | | Temp. ° C. | Alloys, Special | Brass | Bronze | Copper | Iron, Cast | Iron, Special (corrosion) |
|---|---|---|---|---|---|---|---|---|
| Name | Concentration | | | | | | | |
| Acetic anhydride | — | 25 | — | — | — | 0.0002 | — | — |
| | — | 75 | — | — | Best | 0.0040 | — | — |
| Acid, mixed aliphatic | 1.55% calc. as $H_2SO_4$ | 80 | — | 0.0003 | 0.00012 | 0.0012 | — | — |
| Acid, acetic | Glacial | 25 | — | — | — | 0.00020 | — | — |
| | Glacial | 31 | 0.0004 | — | — | — | — | — |
| | Glacial | 50 | — | — | — | 0.0550 | — | — |
| Acid, benzoic vapor | | 250 | — | 0.0146 | — | 0.0075 | 0.0550 | — |
| Acid, chloracetic | Sp. Gr. 1.36 at 50° C. | 100 | — | — | — | 0.0218 | 0.0238 | — |
| Acid, hydrochloric | 35% | 20 | — | — | — | — | — | — |
| | — | 100 | — | — | — | — | — | — |
| | 27% | 20–30 | — | — | — | — | 0.36 | 0.0075 |
| | — | 80–88 | — | — | — | — | Infin. | 0.124 |
| | 20 | 20–25 | — | — | — | — | — | — |
| | — | 100 | — | — | — | — | — | — |
| | 10 | 20–30 | — | — | — | — | 0.256 | 0.001 |
| | 10 | 70 | — | — | — | — | — | — |
| | Saturated with $PbCl_2$ 10% | 70 | — | — | — | — | — | — |
| | — | 80–100 | — | — | — | — | Infin. | 0.014 |
| | 5 | | | | | | | |

## SUMMARY

| Solution | | Temp. ° C. | Lead | Lead, Special Hard | Monel Metal | Nickel | Steel, Medium | Steel, Mild | Zinc |
|---|---|---|---|---|---|---|---|---|---|
| Name | Concentration | | | | | | | | |
| Acetic anhydride | — | 25 | 0.002 | — | — | — | — | — | — |
| | — | 75 | 0.006 | — | — | — | — | — | — |
| Acid, mixed aliphatic | 1.55% calc. as $H_2SO_4$ | 80 | 0.0044 | — | 0.0002 | — | — | 0.0067 | — |
| Acid, acetic | Glacial | 25 | — | — | — | — | — | 0.0056 | — |
| | Glacial | 31 | — | — | — | — | — | — | — |
| | Glacial | 50 | — | — | — | — | — | — | — |
| | Glacial, 98.0% | 25 | 0.007 | — | — | — | — | 0.0051 | — |
| | Glacial, 98.0 | 50 | 0.020 | — | — | — | — | 0.1 | — |
| | 99.5% +5% $S_2Cl_2$ | 25 | 0.0002 | — | — | — | — | 0.028 | — |
| | Glacial, 99.5 +5% $S_2Cl_2$ | 50 | 0.001 | — | — | — | — | 0.080 | — |
| Acid, acetic | | 70 | 0.0006 | — | — | — | — | — | — |
| Acid, acetic | Saturated with lead acetate | 70 | 0.0024 | — | — | — | — | — | — |
| Acid, acetic | 79.9% | 25 | 0.0066 | — | — | — | — | — | — |
| Acid, acetic | 79.9%, saturated with $Na_2SO_4$ | 25 | 0.0044 | — | — | — | — | — | — |
| Acid, benzoic vapor | — | 250 | — | — | 0.0032 | 0.0022 | — | 0.0596 | 0.0445 |
| Acid, chloracetic | Sp. Gr. 1.36 at 50° C. Plant | 100 | 0.0547 | — | — | 0.0019 | — | 0.0315 | — |
| Acid, hydrochloric | 35% | 20 | 0.091 | 0.0010 | — | — | — | — | — |
| | | 100 | 0.172 | 0.0024 | — | — | — | — | — |
| | 27 | 20–30 | — | — | — | — | 0.4 | — | — |
| | — | 80–88 | — | — | — | — | Infin. | — | — |
| | 20 | 20-25 | 0.006 | — | — | — | — | — | — |
| | — | 100 | 0.120 | — | — | — | — | — | — |
| | 10 | 20–30 | 0.001 | 0.0002 | — | — | 0.4 | — | — |
| | 10 | 70 | 0.0138 | — | — | — | Infin. | — | — |
| | Saturated with $PbCl_2$ 10% | 70 | 0.0105 | — | — | — | — | — | — |
| | — | 80–100 | 0.013 | 0.0006 | — | — | — | — | — |
| | 5% | 20–25 | 0.0015 | 0.0001 | — | — | — | — | — |
| | — | 100 | 0.0045 | 0.0006 | — | — | — | — | — |
| | 2 | 100 | — | — | 0.0019 | — | — | — | — |
| | 1% +alizarin | 100 | — | — | 0.0085 | — | — | — | — |
| | 1% | 20–25 | 0.001 | 0.0001 | — | — | — | — | — |
| | 1% — | 100 | 0.003 | 0.0001 | — | — | — | — | — |
| Acid, mixed | Sulphuric 20%, hydrochloric 0% | 25 | 0.0001 | | | | | | |

| Solution | | Temp. ° C. | Alloys Special | Aluminum | Iron, Cast | Iron, Special (corrosiron) |
|---|---|---|---|---|---|---|
| Name | Concentration | | | | | |
| Acid, nitric | 90% | 25 | 0.13 | — | 0.0345 | 0.0000 |
| | 70% | 25 | 0.14 | 0.0031 | — | — |
| | | 80–88 | — | — | 0.49 | 0.0001 |
| | 30% | 25 | 0.08 | — | — | — |
| | 10% | 20–30 | — | — | 0.315 | 0.0000 |
| | — | 80–88 | — | — | 0.611 | 0.0001 |
| Acid, sulphuric | Oleum | 20–30 | — | — | 0.0013 | 0.003 |
| | | 80–88 | — | — | 0.0139 | 0.085 |
| | 99% | 40 | — | — | 0.010 | — |
| | — | 25 | 0.005 | — | — | — |
| | 93% | 20–30 | — | — | 0.0015 | 0.0000 |

## SUMMARY

| Solution | | | Temp. ° C. | Lead | Steel, Medium | Steel, Mild |
|---|---|---|---|---|---|---|
| Name | Concentration | | | | | |
| Acid, mixed | Sulphuric 18%, hydrochloric 2% | | 25 | 0.0032 | — | — |
| | 15 | 5 | 25 | 0.0179 | — | — |
| | 10 | 10 | 25 | 0.0489 | — | — |
| | 5 | 15 | 25 | 0.0856 | — | — |
| | 2 | 18 | 25 | 0.1326 | — | — |
| | Sulphuric 20%, nitric | 0 | 25 | 0.2478 | — | 2.8 |
| | 2 to 18 | 2 to 18 | 25 | Very great corrosion | — | 8.0-11.0 |
| Acid, nitric | 90% | | 25 | — | 0.1 | — |
| | 70% | | 25 | — | — | — |
| | — | | 80–88 | — | 0.5 | — |
| | 30% | | 25 | — | — | — |
| | 10% | | 20–30 | — | 0.5 | — |
| | — | | 80–88 | — | 1.0 | — |
| | 2% | | 70 | 0.2034 | — | — |
| | 2% sat. with lead nitrate | | 70 | 0.4299 | | |
| Acid, mixed | Sulphuric 8.3%, sodium chloride | 1.7% | 20 | 0.0016 | — | — |
| | | | 100 | 0.0234 | — | — |
| | 16.7 | 3.3 | 20 | 0.0002 | — | — |
| | — | | 100 | 0.0265 | — | — |
| | 31.0 | 17.0 | 20 | 0.0081 | — | — |
| | | | 100 | 0.0369 | — | — |
| | 33.3 | 6.7 | 20 | 0.0007 | — | — |
| | — | | 100 | 0.0148 | — | — |
| | | | 20 | 0.0010 | — | — |
| | 50.0 | 10.0 | 100 | 0.0034 | — | — |
| Acid, sulphuric | Oleum | | 20–30 | — | 0.0017 | — |
| | | | 80–88 | | 0.001–0.2 | — |
| | 105% | | 40 | 0.41 | — | — |
| | — | | 70 | 0.95 | — | — |
| | 99% | | 40 | — | — | 0.0089 |
| | 95% | | 20 | 0.0001 | — | — |
| | — | | 25 | — | — | — |
| | — | | 100 | 0.0041 | — | — |
| | 93% | | 20–30 | — | 0.0018 | — |

| Solution | | Temp. ° C. | Alloy Special | Brass | Copper | Iron, Cast | Iron, Special (corrosion) | Iron, Wrought |
|---|---|---|---|---|---|---|---|---|
| Name | Concentration | | | | | | | |
| Acid, sulphuric | 75% | 31 | 0.0001 | — | — | — | — | — |
| | — | 100 | 0.0004 | — | — | — | — | — |
| | 50% | 20 | — | — | — | — | — | — |
| | — | 100 | — | — | — | — | — | — |
| | 25% | 100 | 0.003 | — | — | — | — | — |
| | 10% | 20–30 | — | — | — | 0.197 | 0.0007 | — |
| | — | 80–88 | — | — | — | 0.248 | 0.0072 | — |
| Caustic soda | — | 100 | — | — | — | — | — | 0.0025 |
| Caustic soda and potash, mixed $\frac{KOH}{NaOH} = \frac{10}{7}$, 25°–50° Bé | | Boiling | — | — | 0.0016 | 0.0491 | — | — |
| Organic materials: Koch's acid, presence of large excess Fe | | 55 | — | — | — | 0.05–0.16 | — | — |
| Green, Malachite, mother liquor | | 80 | — | 0.0002 | — | — | — | — |
| Green, Victoria, mother liquor | | 80 | — | 0.0004 | — | — | — | — |
| Magenta solution plant | | 30–90 | — | — | — | — | — | 0.001–0.01 |
| Mono-nitro-chlorbenzol, plant | | — | — | 0.0021 | — | — | — | — |
| Mono-nitro-chlorbenzol, vapor | | — | — | — | 0.0061 | — | — | — |
| Mono-nitro-chlorbenzol, dehydrated | | — | — | — | — | 0.0009 | — | 0.0008 |
| Para-nitrophenol, saturated | | 40 | — | — | 0.0004 | — | — | — |
| | | 100 | — | — | 0.0006 | — | — | — |

## SUMMARY

| Solution | | Temp. ° C. | Lead | Lead, Special Hard | Monel Metal | Nickel | Steel, Med. | Steel, Mild |
|---|---|---|---|---|---|---|---|---|
| Name | Concentration | | | | | | | |
| Acid, sulphuric | 50% | 20 | 0.00001 | — | — | 0.00011 | — | — |
| | | 100 | 0.0002 | — | — | — | — | — |
| | 10% | 20–30 | — | 0.00006 | Resists | — | 0.4 | — |
| | | 80–88 | — | 0.00003 | well | — | 0.4 | — |
| | 1 | 20 | — | 0.00002 | — | — | — | — |
| | | 100 | — | 0.00006 | — | — | — | — |
| Caustic soda | 5% | 20 | 0.0011 | — | — | — | — | — |
| | | 100 | 0.0035 | — | — | — | — | — |
| | 25% | 20 | 0.0004 | — | — | — | — | — |
| | | 100 | 0.0010 | — | — | — | — | — |
| | 35% | 20 | 0.0003 | — | — | — | — | — |
| | | 100 | 0.0005 | — | — | — | — | — |
| Lead acetate | — | — | 0.0783 | — | — | — | — | — |
| Organic materials: 1.5 oxy acid process | | — | 0.079 | — | — | — | — | — |
| Brown acid | | 35–50 | — | — | 0.03 | — | — | — |
| H-acid nitration mixture | | 30–35 | 0.0175 | — | — | — | — | — |
| H-acid nitration mixture + 30% $H_2O$ | | 30–35 | 0.0021 | — | — | — | — | — |
| Koch's acid, presence of large excess Fe | | 55 | 0.00005 | — | — | — | — | — |
| Presence small am't. Fe | | 55 | 0.00005 | — | — | — | — | — |
| No Fe present | | 25–50 | 0.0004 | — | 0.04 | — | — | 0.01–0.03 |
| Green, Malachite, mother liquor | | 80 | 0.00005 | — | — | — | — | Very slight |
| Green, Victoria, mother liquor | | 80 | 0.0006 | — | — | — | — | — |
| Mono-nitro-chlorbenzol, vapor | | — | Disintegrated | — | — | — | — | — |
| Mono-nitro-chlorbenzol, dehydrated | | -- | — | — | — | — | 0.0006 | — |
| Para-nitrophenol, saturated sol. | | 40 | 0.0025 | — | — | — | — | — |
| | | 100 | 0.0042 | — | — | — | — | — |

| Solution | | Temp. ° C. | Copper | Iron, Cast | Iron, Wrought |
|---|---|---|---|---|---|
| Name | Concentration and Description | | | | |
| Pontachrome brown | — | 75 | — | 0.007 | — |
| Sodium hydrosulphite | 20% solution | 25 | — | 0.0081 | — |
| Sodium hypochlorite | — | 25 | 0.0003 | — | — |
| Water, river, Delaware | | | | | 0.001 |

## SUMMARY

| Solution | | Temp. ° C. | Lead | Nickel | Steel, Mild | Zinc |
|---|---|---|---|---|---|---|
| Name | Concentration and Description | | | | | |
| Benzaldehyde | — | 40 | — | — | — | 0.006 |
| Phenylglycine | Ferrous mother liquor | 25–75 | — | 0.0001 | — | — |
| Pontachrome brown | — | 75 | — | — | — | — |
| Sodium hydrosulphite | 20% solution | 25 | 0.00007 | — | 0.0030 | — |
| Sodium hypochlorite | | 25 | 0.1280 | — | 0.00003 | — |
| Sodium sulphide | 5% | 25 | 0.002 | — | — | — |
| | | — | 0.001 | — | — | — |
| | 10, 15, 20 and 25% | 25 | 0.001 | — | — | — |
| | 10, 15, 20 and 25% | 100 | 0.001 | — | — | — |
| Water, river, Delaware | | — | — | — | 0.001 | 0.001 |

## TABLE IX

### Corrosion of Metals by Vapors

| Metal | | Vapor | | Laboratory Test | | Rate of Corrosion |
|---|---|---|---|---|---|---|
| Name | Description | Name | Desc. or Conc. | Temp. ° C. | Method No. | Inches Penetration per Month |
| Brass | Yellow (1) | Benzoic acid | | 250 | 1 | 0.0146 |
| Brass | Yellow | Mono-nitrochlor-benzol | | | 2 | 0.0003 |
| Copper | Hardness +21(3) | Benzoic acid | Plant product | 250 | 1 | 0.0075 |
| Copper | | Mono-nitrochlor-benzol | | | 2 | 0.0061 |
| Iron | Cast, hardness =8 | Benzoic acid | " " | 250 | 1 | 0.0550 |
| Lead | | Mono-nitrochlor-benzol | | | 2 | Completely disintegrated |
| Monel | Hardness =20 | Benzoic acid | " " | 250 | 1 | 0.0032 |
| Nickel | Hardness =30 | Benzoic acid | " " | 250 | 1 | 0.0022 |
| Sodium silicate coating on mild steel (8) | | Benzoic acid | " " | 250 | 1 | 0.00622 |
| Sodium silicate coating on cast iron (9) | | " " | " " | 250 | 1 | 0.00472 |
| Steel, mild, hardness =23 | | " " | " " | 250 | 1 | 0.0596 |

Remarks:

1. Differential removal of zinc by vapor.
3. Hardness =11 after test.
8. Corrosion of metal reported.
9. Corrosion of metal reported.

## TABLE X

### Corrosion of Enamels and Coatings by Solutions and Vapors

| Enamel or Coating | Solution or Vapor | Time of Exposure | Temp. ° C. | Results |
|---|---|---|---|---|
| Bakelite protective enamel No. 6 on steel cup | Acid, (wood digestion in alcohol plant), 1.55% calc. as $H_2SO_4$ | 8 days (8 hrs. each day) | 80 | Blistered and broke, exposing metal |
| Bakelite (baked) on steel | Acid, acetic 83.4% | 5 days | 25–30 | Blistered and broke upon drying after test. Otherwise protected. |
| Enamel, Elyria blue | Acid, 5% $HNO_2$+$HNO_3$ +$Hg(NO_3)_2$ | 28 days | 25 | No visible action |
| Enamel, Limberg Foundry Co. | Acid, 5% $HNO_2$+$HNO_3$ +$Hg(NO_3)_2$ | " " | 25 | Very slight action |
| Enamel, Stuart & Peterson | Acid, 5% $HNO_2$+$HNO_3$ +$Hg(NO_3)_2$ | " " | 25 | Almost completely destroyed |
| Iron, galvanized | Benzaldehyde, 1.58% impurity | 24 hrs. | 40 | 0.0404" penetration per month |
| " " | " 9.55% " | " " | 40 | 0.0017 " " " |
| Sodium silicate on cast iron | Benzoic acid vapor | 12 hrs. | 250 | 0.00622 " " " |
| Sodium silicate on mild steel | " " " | " " | 250 | 0.00472 " " " |
| *Thermometer scales:* | | | | |
| Acid, proof, SP 35, | HCl acid fume | 1.25 hrs. | 25 | Attacked slightly |
| A. Weiskopf, Chicago | " " " | | | |
| Acid proof, SP, 60, | " " " | | | |
| A. Weiskopf, Chicago | " " " | 1.25 hrs. | 25 | Almost completely destroyed |

## TABLE XI

### Deterioration of Woods

| Wood | Density (before testing) lb./cu. ft. | Increase in Weight | Increase in Volume | Increase in Density |
|---|---|---|---|---|
| | | % | % | % |
| *Very Hard* | | | | |
| Ebony* | 71 | 7 | 7 | 0 |
| Lignum Vitae | 83 | −2 | 11 | −12 |
| *Hard* | | | | |
| Ash† | 45 | 85 | 12 | 67 |
| Beech† | 49 | 66 | 11 | 49 |
| Birch, White† | 41 | 79 | 8 | 63 |
| Maple, Rock† | 43 | 70 | 8 | 58 |
| Oak, White | 44 | 54 | 0.7 | 52 |
| Average | 45 | 71 | 8 | 58 |
| *Soft* | | | | |
| Cypress† | 38 | 76 | −1 | 79 |
| Fir† | 45 | 85 | 18 | 58 |
| Pine, Long Leaf, Yellow | 29 | 140 | 5 | 130 |
| Pine, white | 26 | 150 | 0.2 | 158 |
| Spruce | 32 | 99 | 8 | 88 |
| Average | 34 | 110 | 6 | 103 |

*Treatment during Test:* 24 hrs. boiling in HCl acid (1%).

*Notes:* Appearance after drying—

* Cracked and warped.

† Warped but no cracks.

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### *Title Abbreviations*

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| | |
|---|---|
| Brit. Pat | British Patent. |
| Dom. Eng | Domestic Engineering. |
| Fr. Pat | French Patent. |
| Ger. Pat | German Patent. |
| Inst. C. E | Institution of Civil Engineers. |
| J. Boston Soc. C. E | *Journal of the Boston Society of Civil Engineers.* |
| J. I. S. I | *Journal of the Iron and Steel Institute.* |
| J. Pharm. Chim. Schweig | |
| Mech. Eng | Mechanical Engineer. |

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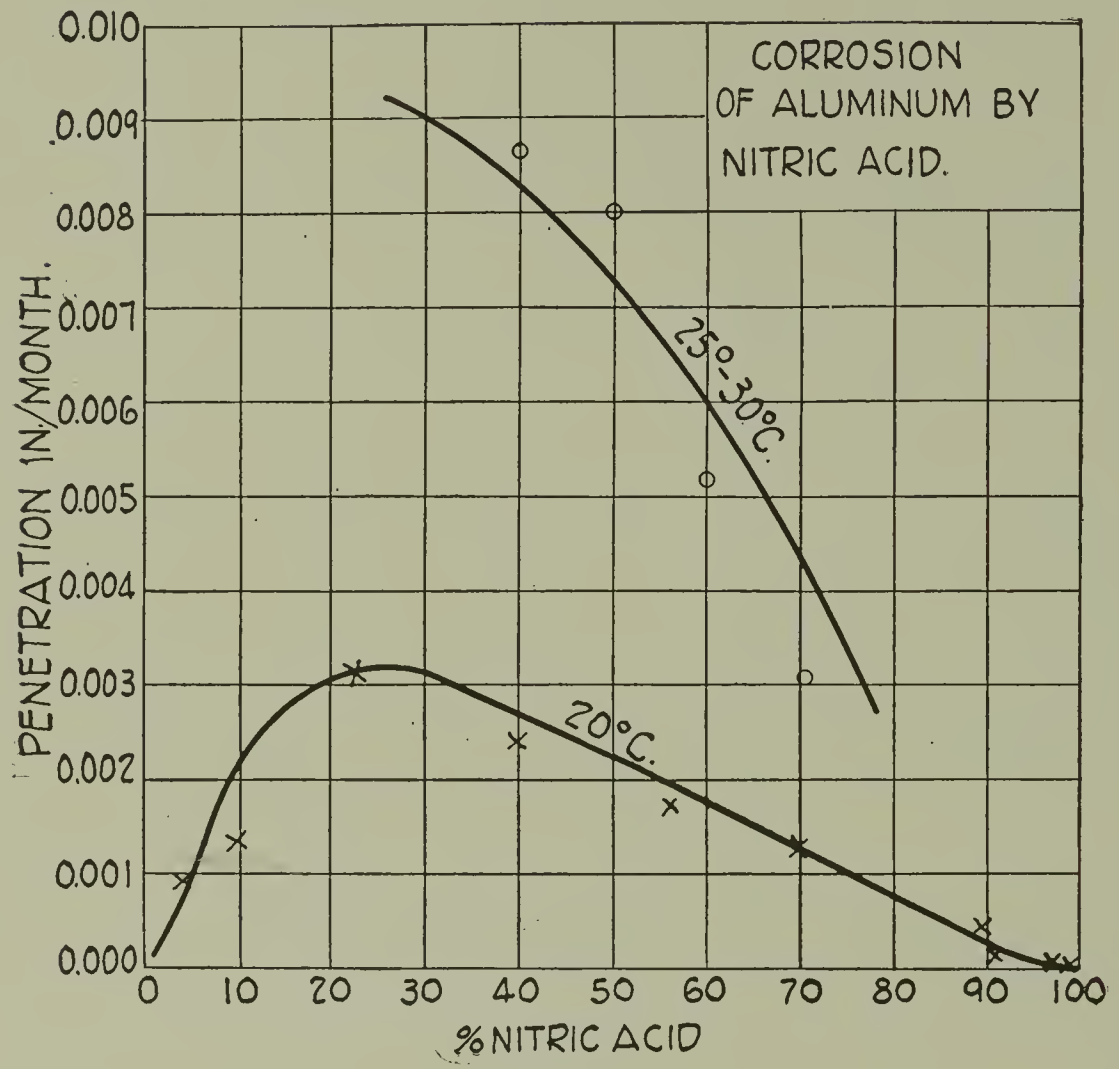
CORROSION
OF ALUMINUM BY
NITRIC ACID.
25°-30°C.
20°C.
PENETRATION IN/MONTH.
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
0 10 20 30 40 50 60 70 80 90 100
% NITRIC ACID

FIG. 1

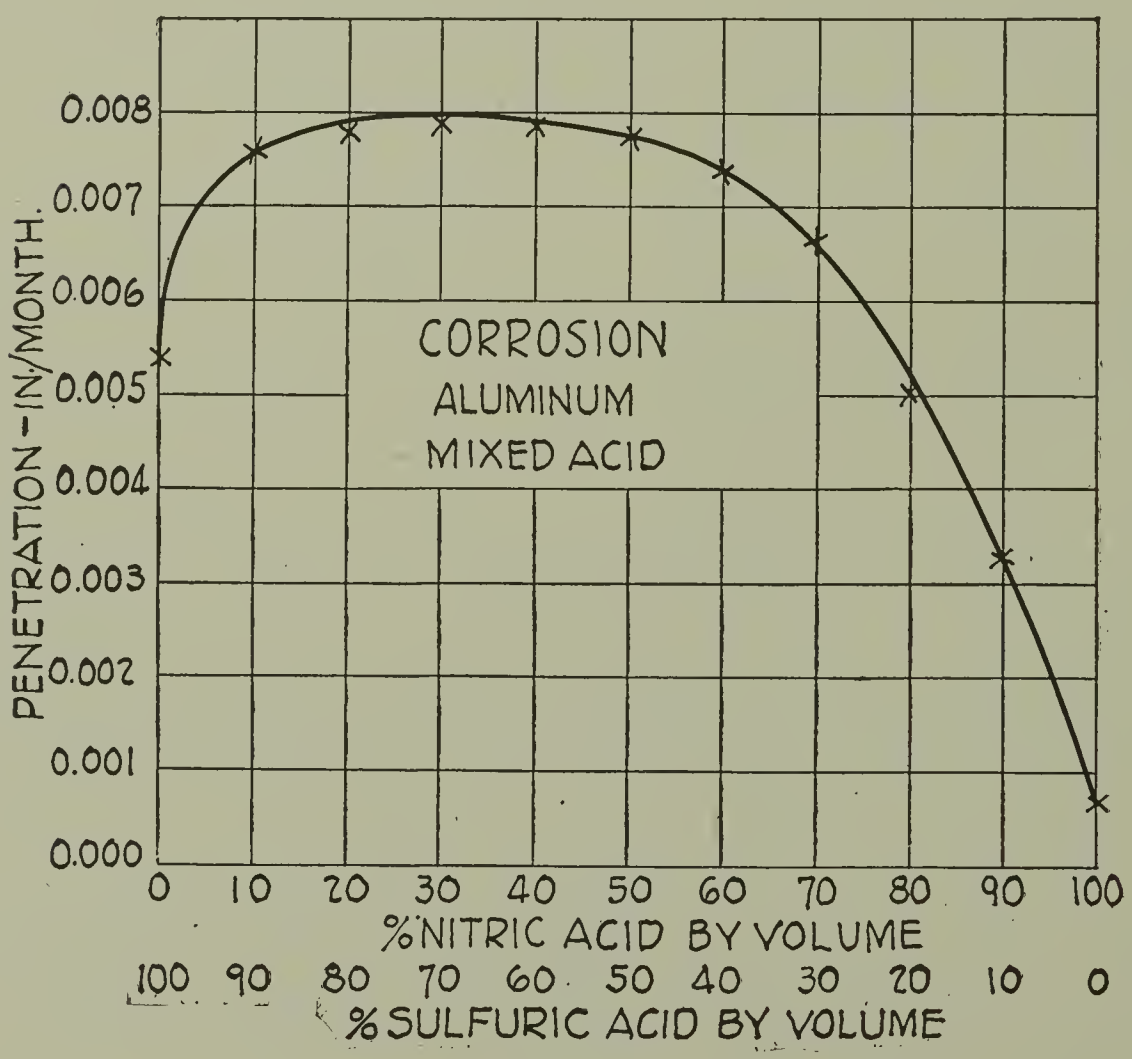
CORROSION
ALUMINUM
MIXED ACID
PENETRATION - IN./MONTH.
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
0 10 20 30 40 50 60 70 80 90 100
% NITRIC ACID BY VOLUME
100 90 80 70 60 50 40 30 20 10 0
% SULFURIC ACID BY VOLUME

FIG. 2

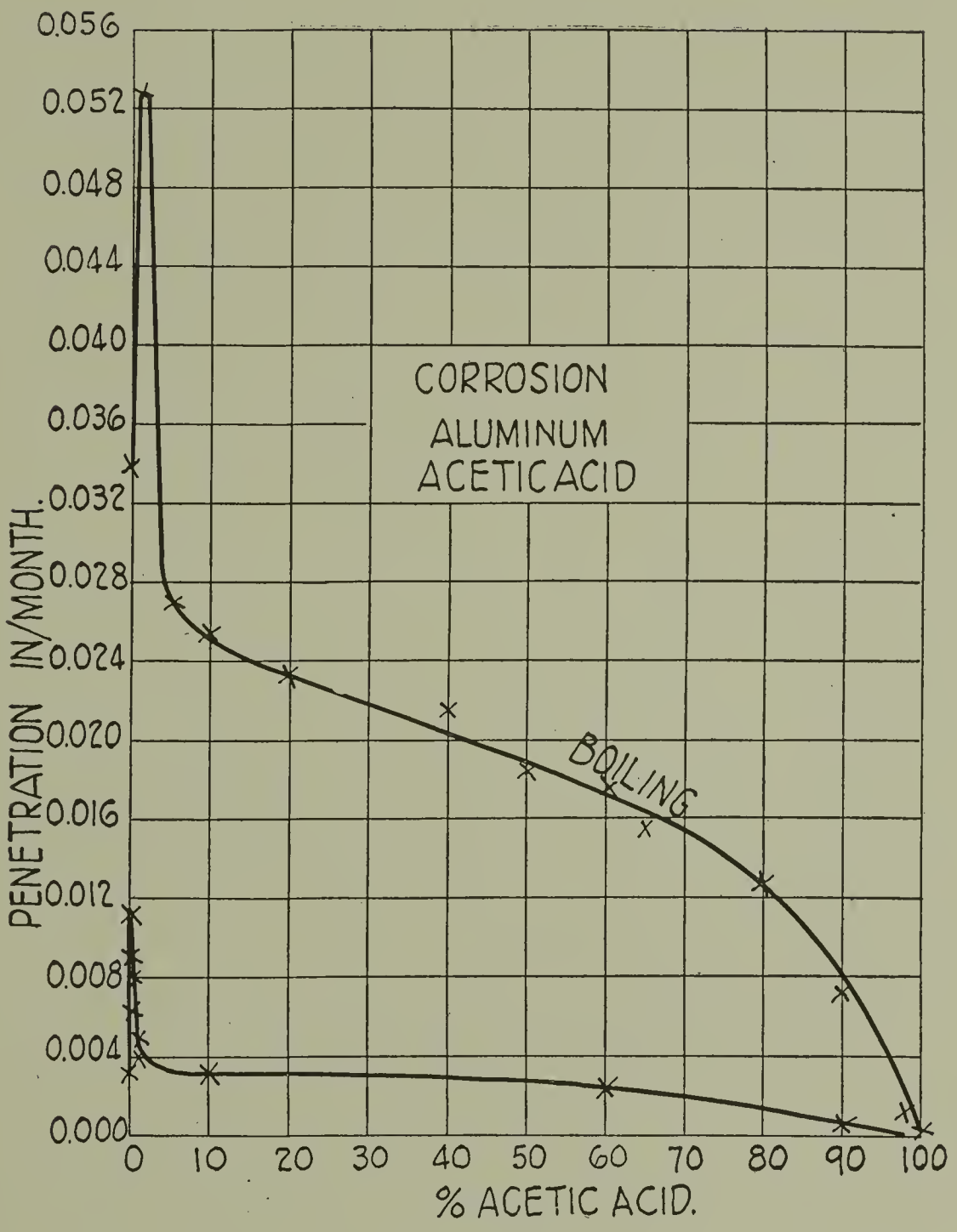
0.056
0.052
0.048
0.044
0.040
0.036
0.032
0.028
0.024
0.020
0.016
0.012
0.008
0.004
0.000
PENETRATION IN/MONTH.
CORROSION
ALUMINUM
ACETIC ACID
BOILING
0 10 20 30 40 50 60 70 80 90 100
% ACETIC ACID.

FIG. 3

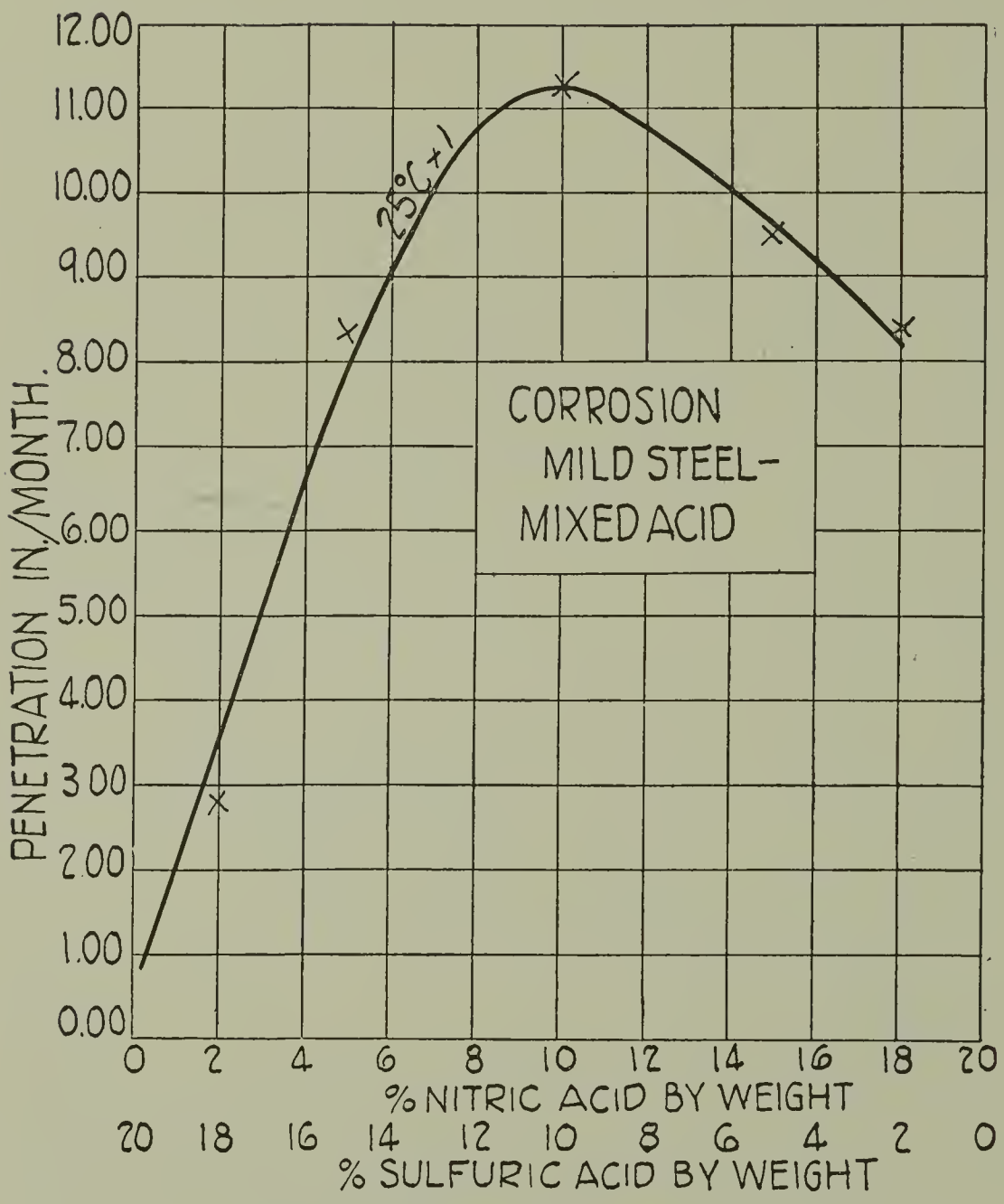
12.00
11.00
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
PENETRATION IN./MONTH.
25°C.±1
CORROSION
MILD STEEL-
MIXED ACID
0 2 4 6 8 10 12 14 16 18 20
% NITRIC ACID BY WEIGHT
20 18 16 14 12 10 8 6 4 2 0
% SULFURIC ACID BY WEIGHT

FIG. 4

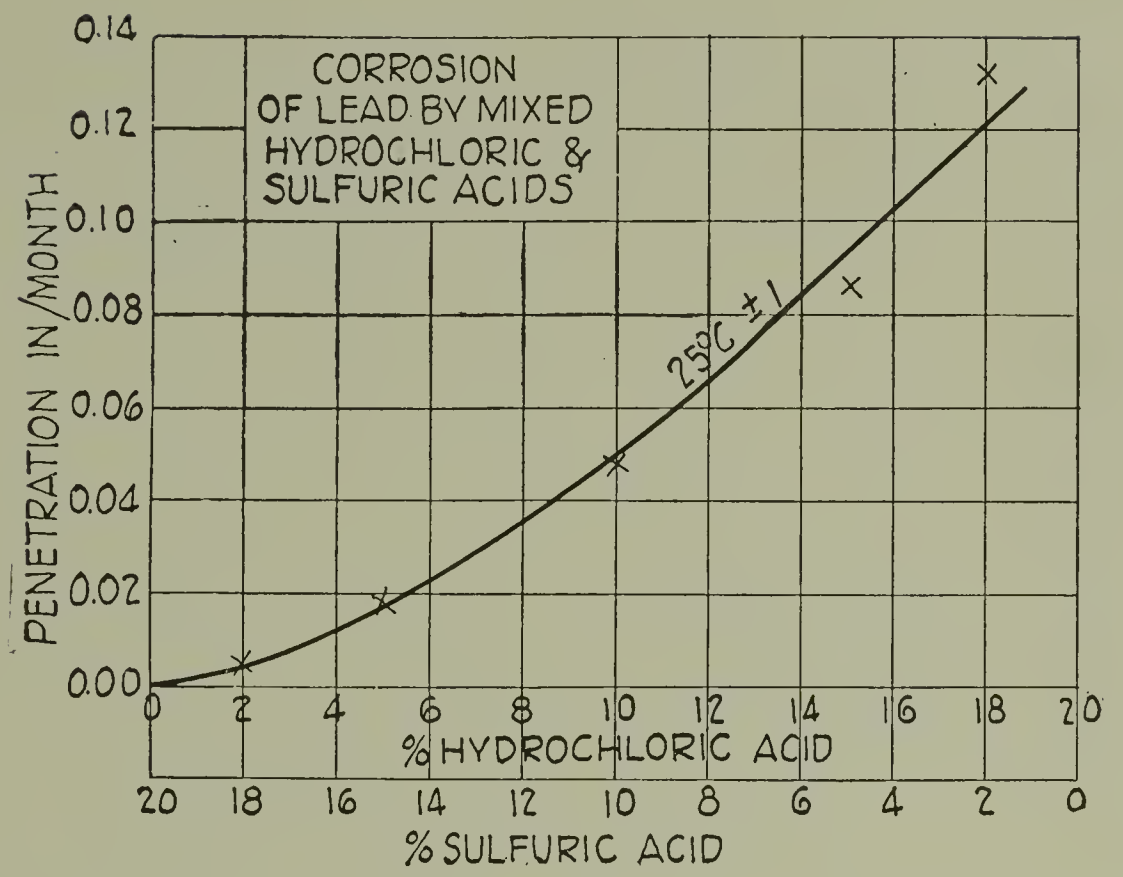
CORROSION
OF LEAD BY MIXED
HYDROCHLORIC &
SULFURIC ACIDS
25°C ± 1
PENETRATION IN/MONTH
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0 2 4 6 8 10 12 14 16 18 20
% HYDROCHLORIC ACID
20 18 16 14 12 10 8 6 4 2 0
% SULFURIC ACID

FIG. 5

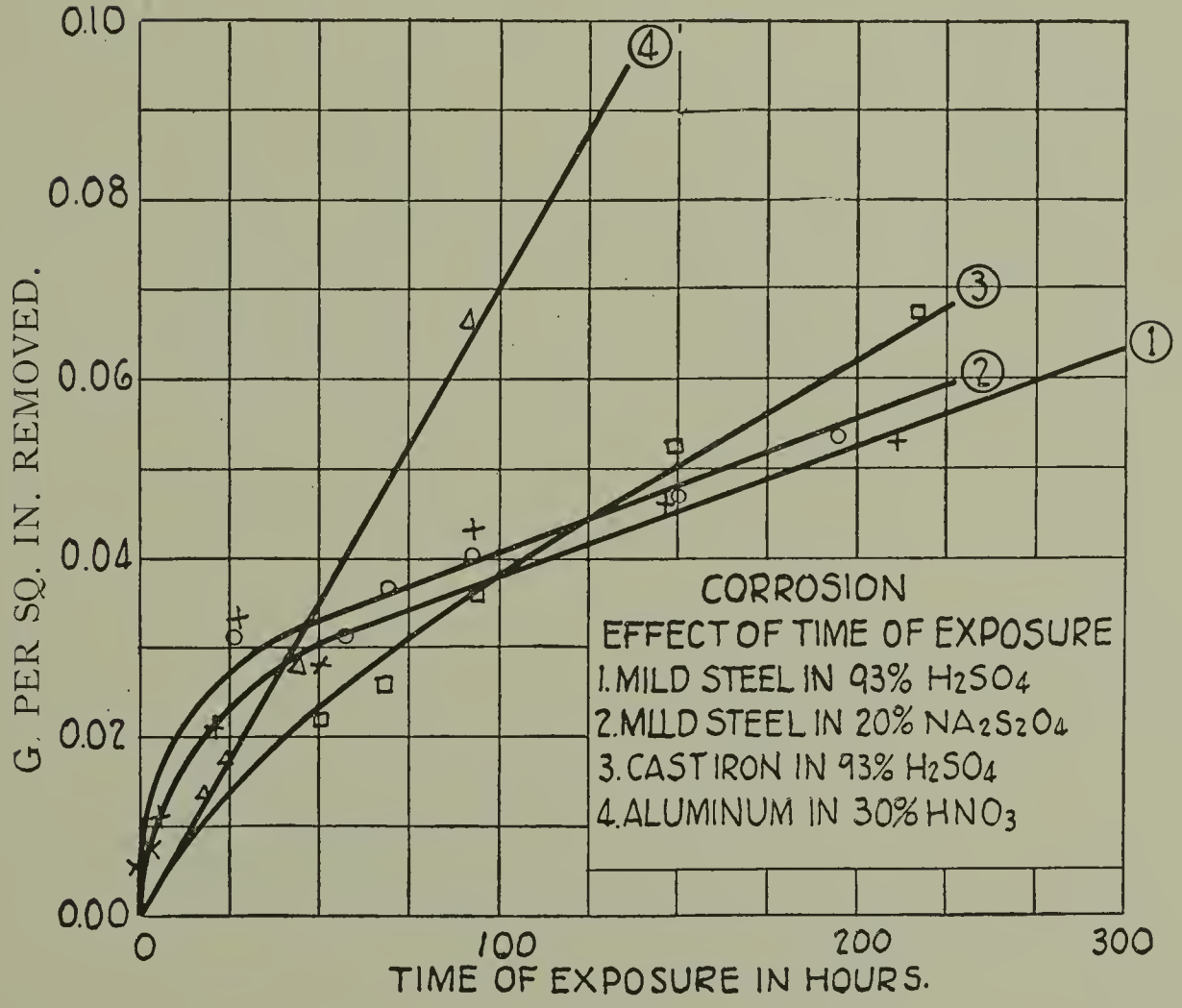
G. PER SQ. IN. REMOVED.
0.10
0.08
0.06
0.04
0.02
0.00
0
100
200
300
TIME OF EXPOSURE IN HOURS.
CORROSION
EFFECT OF TIME OF EXPOSURE
1. MILD STEEL IN 93% $H_2SO_4$
2. MILD STEEL IN 20% $NA_2S_2O_4$
3. CAST IRON IN 93% $H_2SO_4$
4. ALUMINUM IN 30% $HNO_3$
①
②
③
④

FIG. 6

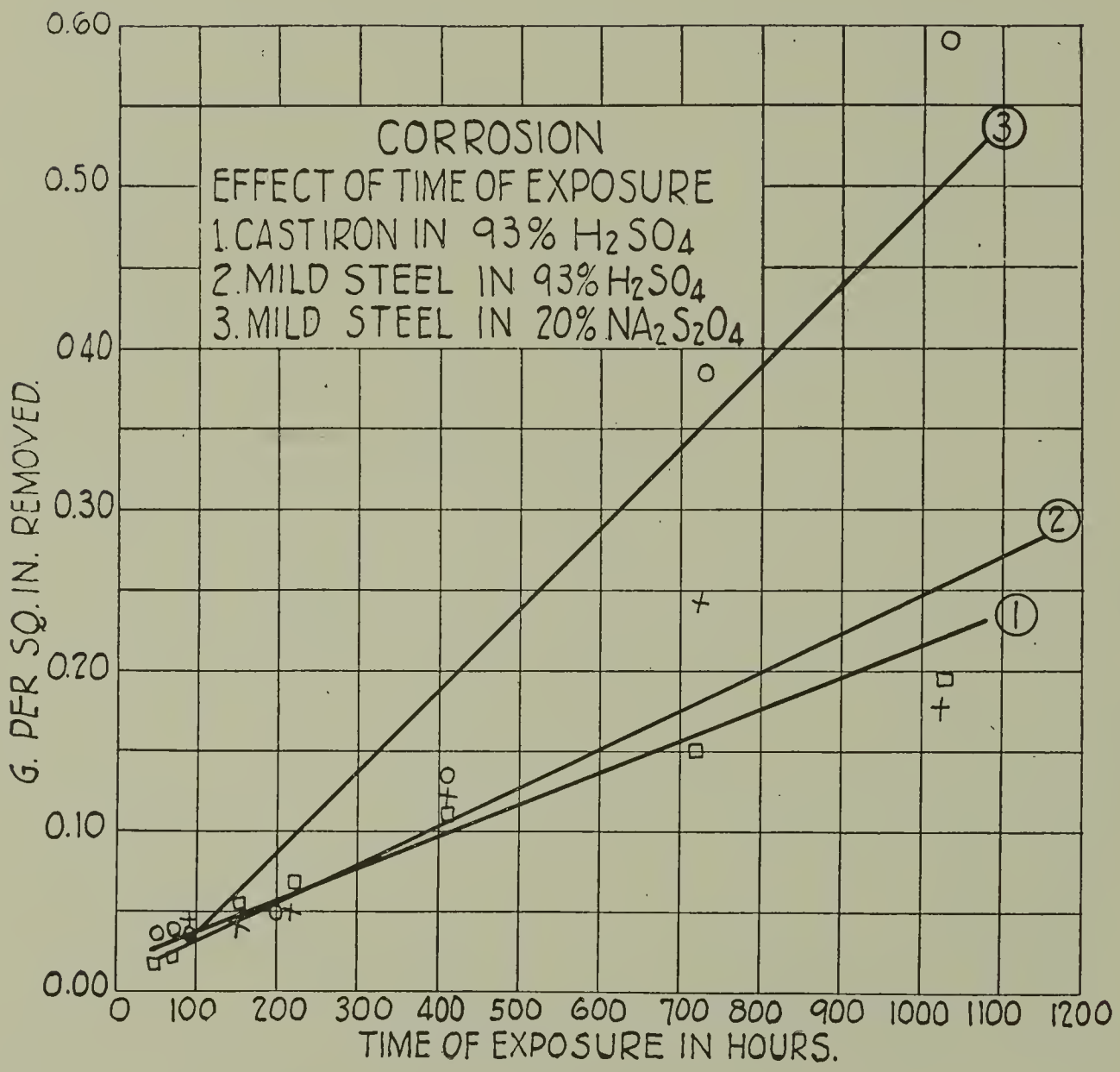
CORROSION
EFFECT OF TIME OF EXPOSURE
1. CAST IRON IN 93% $H_2SO_4$
2. MILD STEEL IN 93% $H_2SO_4$
3. MILD STEEL IN 20% $NA_2S_2O_4$
G. PER SQ. IN. REMOVED.
0.60
0.50
040
0.30
0.20
0.10
0.00
0 100 200 300 400 500 600 700 800 900 1000 1100 1200
TIME OF EXPOSURE IN HOURS.
1
2
3

FIG. 7

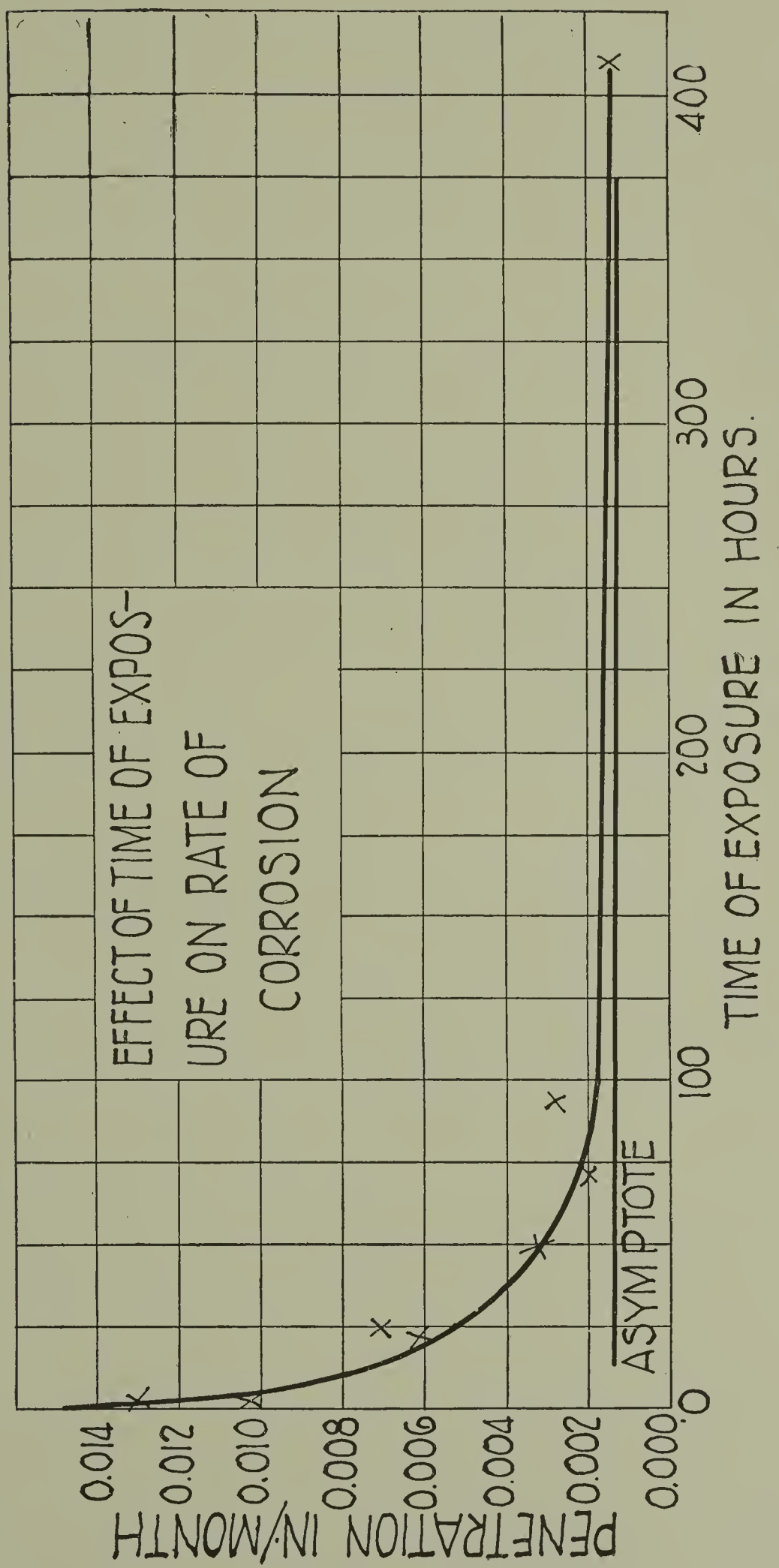
EFFECT OF TIME OF EXPOS-
URE ON RATE OF
CORROSION
PENETRATION IN/MONTH
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
0
100
200
300
400
TIME OF EXPOSURE IN HOURS.
ASYMPTOTE
X

FIG. 8

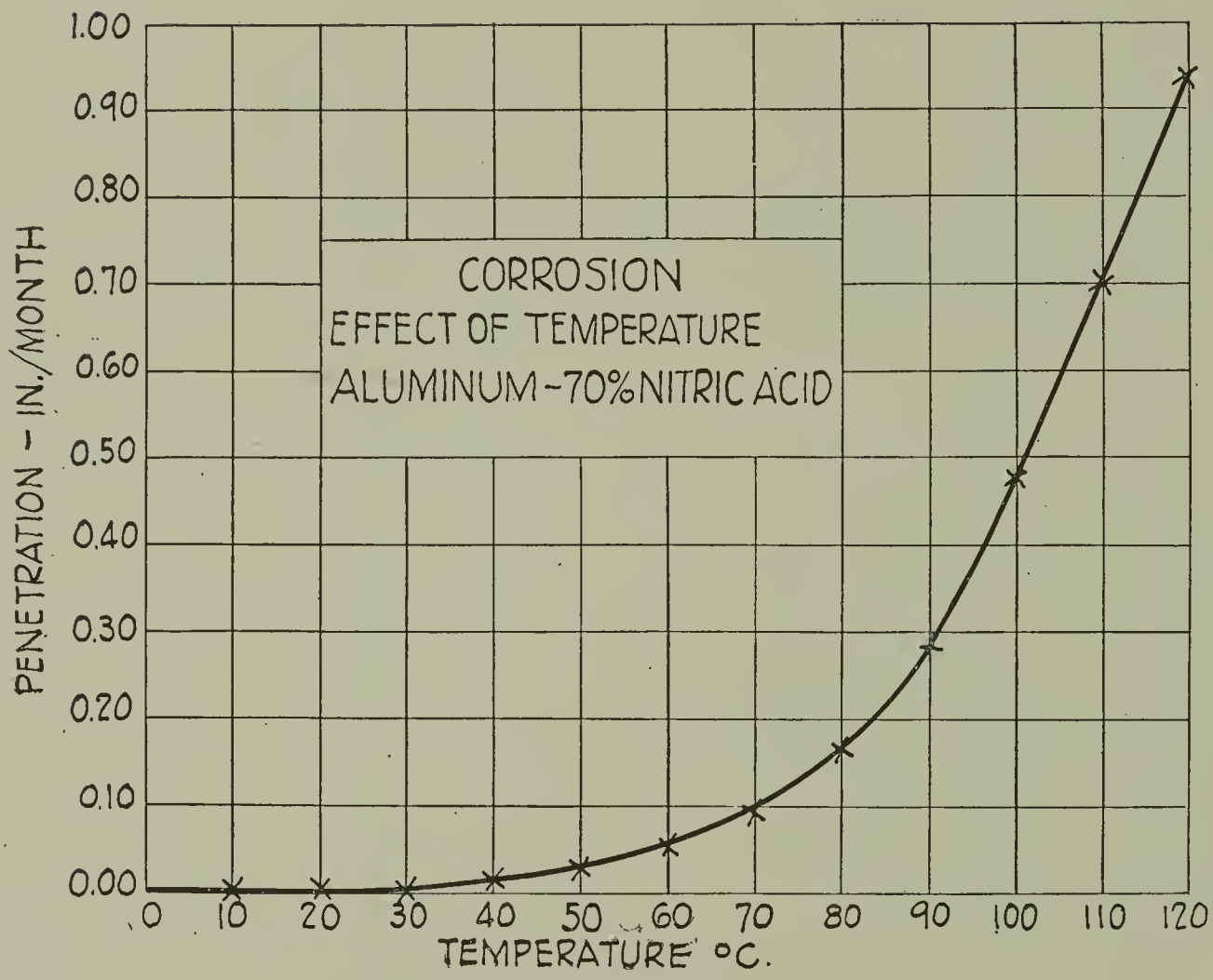
CORROSION
EFFECT OF TEMPERATURE
ALUMINUM - 70% NITRIC ACID
PENETRATION - IN./MONTH
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0
10
20
30
40
50
60
70
80
90
100
110
120
TEMPERATURE °C.

FIG. 9

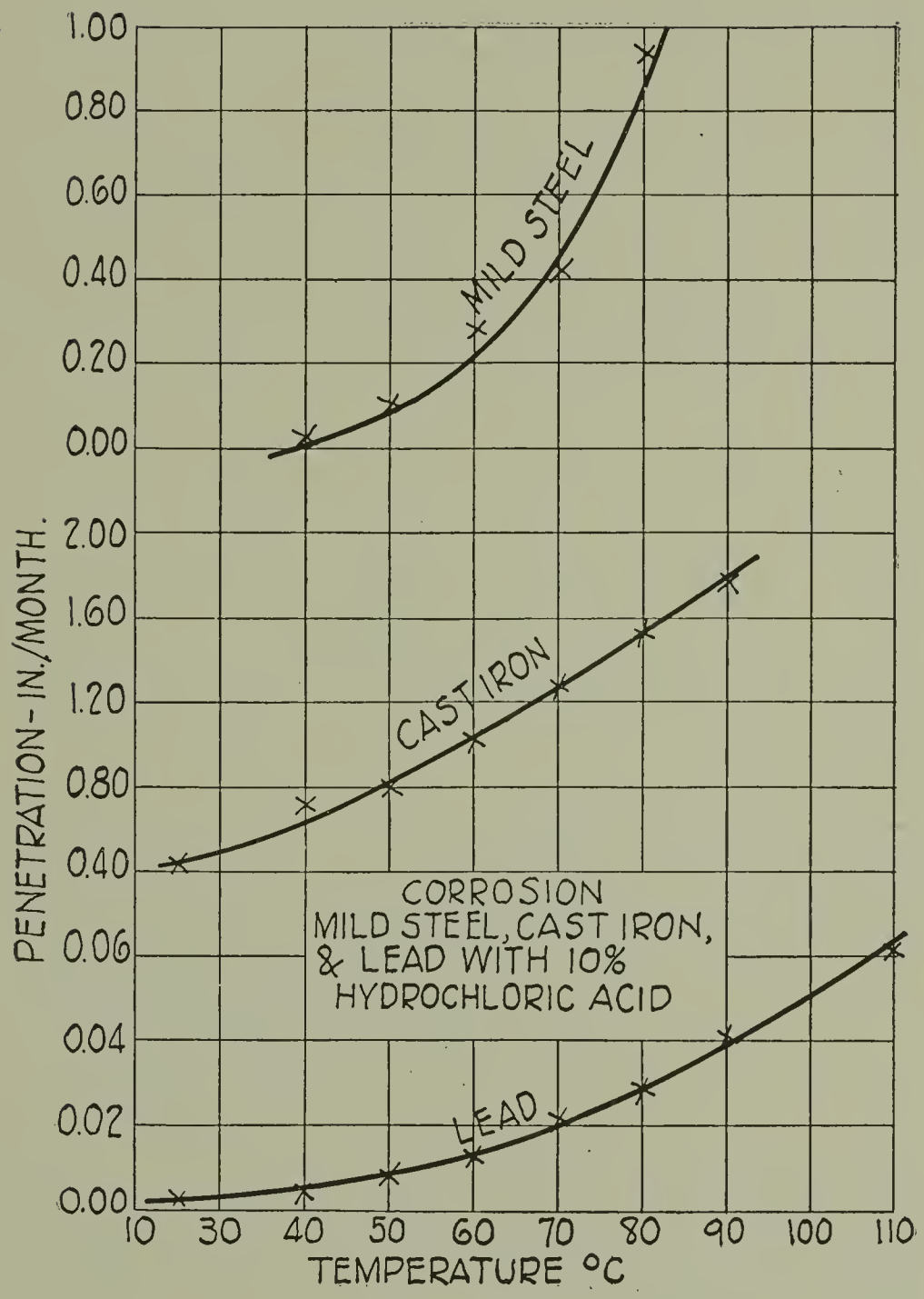
1.00
0.80
0.60
0.40
0.20
0.00
2.00
1.60
1.20
0.80
0.40
0.06
0.04
0.02
0.00
PENETRATION-IN./MONTH.
MILD STEEL
CAST IRON
LEAD
CORROSION
MILD STEEL, CAST IRON,
& LEAD WITH 10%
HYDROCHLORIC ACID
10 30 40 50 60 70 80 90 100 110
TEMPERATURE °C

FIG. 10

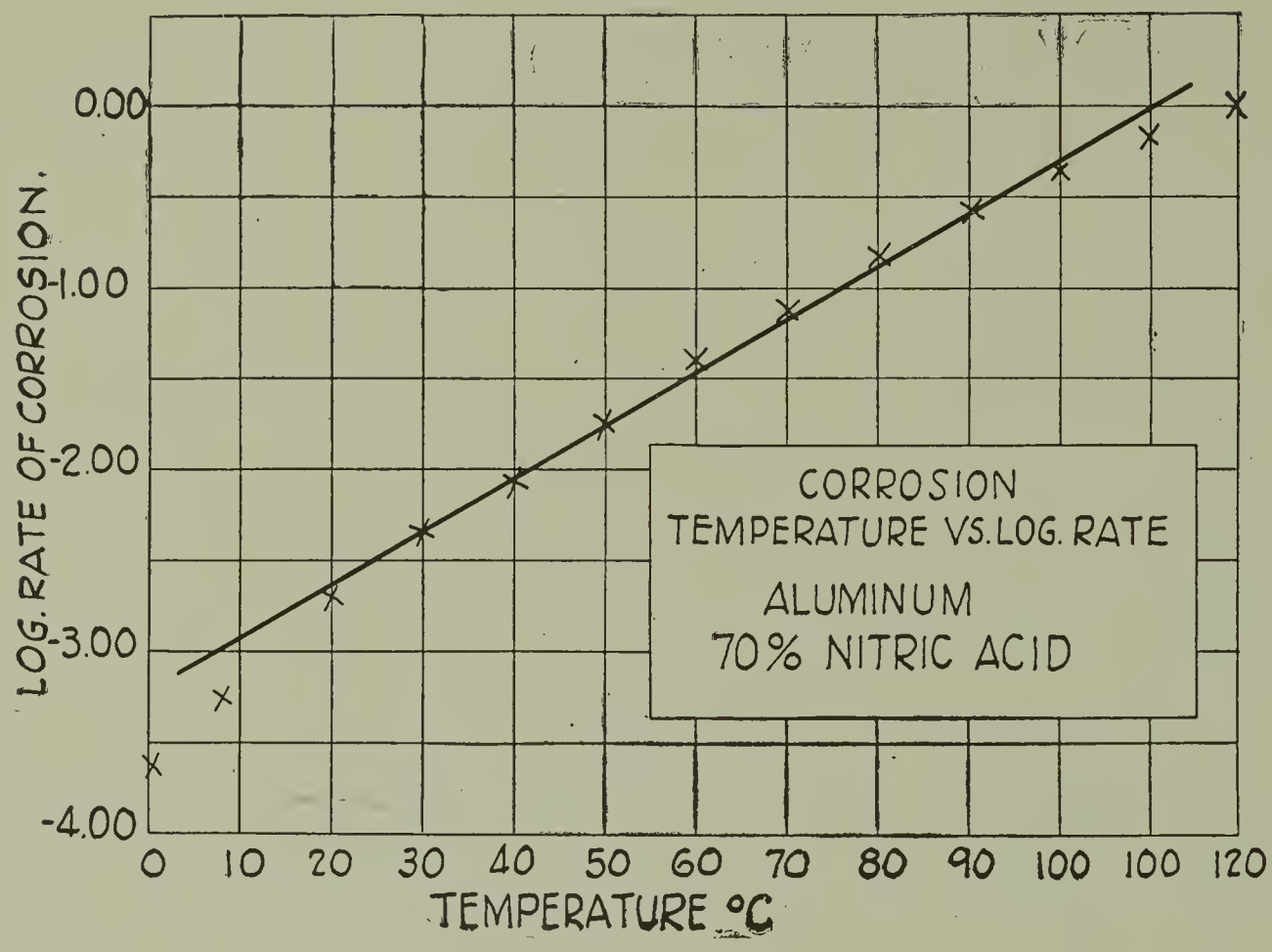
0.00
-1.00
-2.00
-3.00
-4.00
LOG. RATE OF CORROSION.
0 10 20 30 40 50 60 70 80 90 100 100 120
TEMPERATURE °C
CORROSION
TEMPERATURE VS. LOG. RATE
ALUMINUM
70% NITRIC ACID

FIG. 11

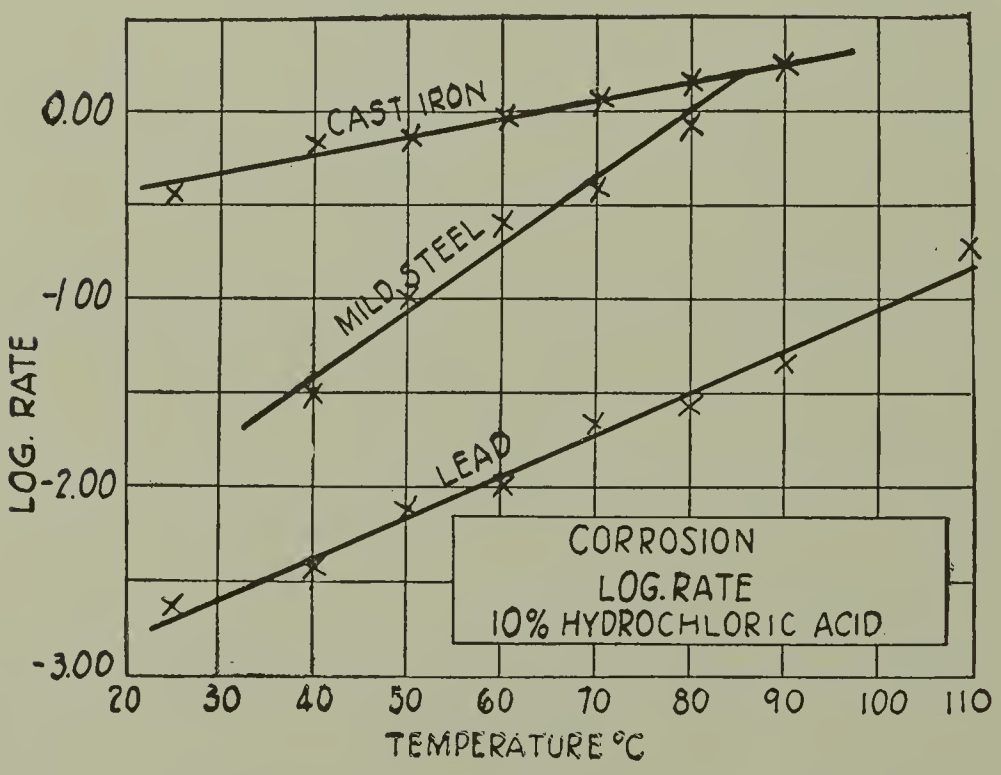
0.00
-1.00
-2.00
-3.00
LOG. RATE
CAST IRON
MILD STEEL
LEAD
20 30 40 50 60 70 80 90 100 110
TEMPERATURE °C
CORROSION
LOG. RATE
10% HYDROCHLORIC ACID

FIG. 12

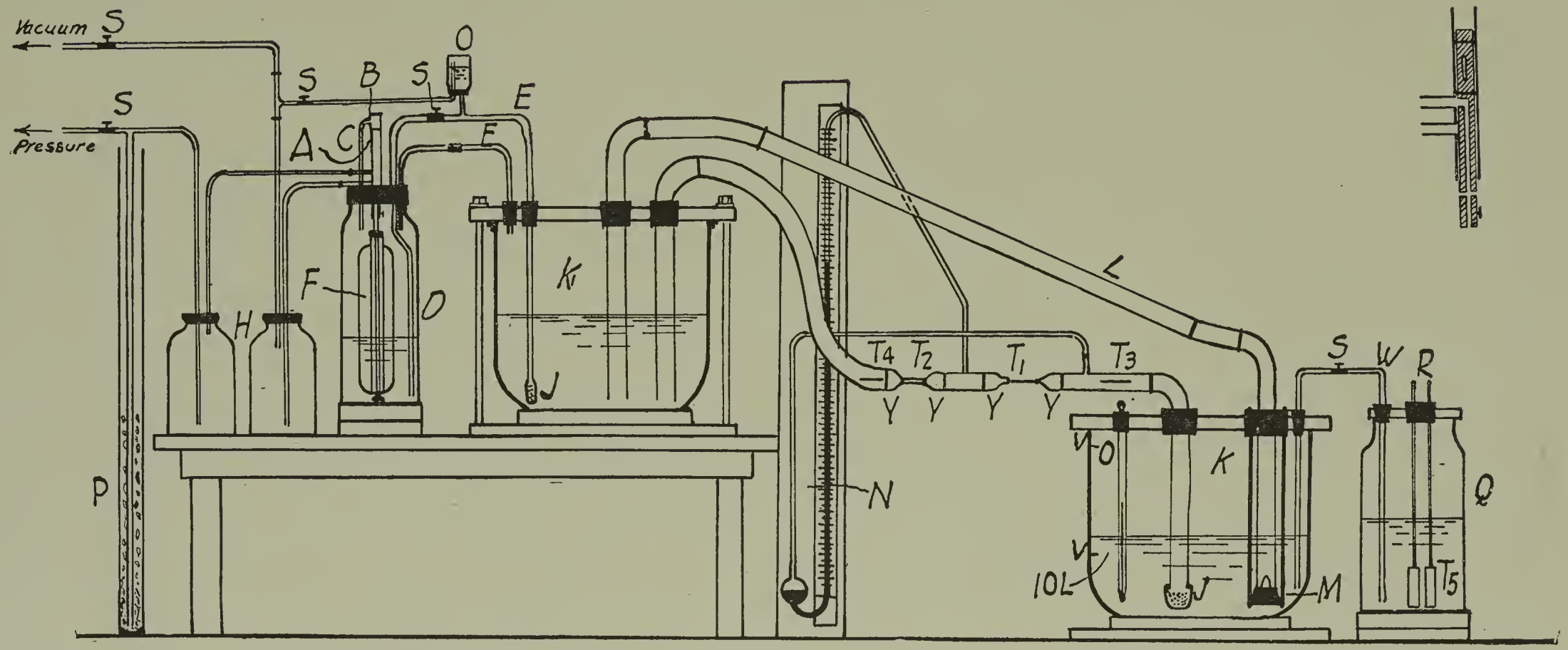


FIG. 13. Apparatus for corrosion tests under velocity conditions (0–2,000 ft./min.). *A*, air valve; *B*, air valve oil cup; *C*, air valve pressure equalization tube; *D*, float chamber; *E*, siphon; *F*, glass float; *G*, air tube; *H*, traps; *J*, glass wool filter; *K*, corrosive liquid containers (*K*, air-tight cover); *L*, return tube for corrosive liquid; *M*, glass and rubber check valve; *N*, vacuum gauge; *O*, bottle for air removal from siphon; *P*, pressure regulator ($Hg - H_2O$); *Q*, overflow bottle; *R*, glass support hooks for test pieces; *S*, screw clamps; *V*, volume calibration (10L); *W*, siphon; *Y*, glass reducers; $T_1$, small diameter test-tube (high $v$); $T_2$, large diameter test-tube (medium $v$); $T_3$, test piece (low $v$, atmospheric); $T_4$, test piece (low $v$, vacuum); $T_5$, test piece (zero $v$).

# MATERIALS OF CONSTRUCTION FOR CHEMICAL APPARATUS

By HAROLD F. WHITTAKER

Chemical Engineer National Research Council, Washington, D. C.

Read and discussed at the Wilmington Meeting, June 22, 1923

Until the latter half of the nineteenth century, designers of apparatus were influenced chiefly by two considerations; namely, material cost and material strength.

Owing to the great abundance of iron ore deposits, their easy conversion to the metal, the consequent low price for iron and steel, and their great strength, this metal has always been given first consideration when construction was contemplated. On the other hand, experience has shown that iron and steel are not permanent, even when well protected from atmospheric or other corrosive conditions. In spite of this, iron and steel have held their own, and are to-day the principal materials of construction.

With the development of the chemical industry, it became necessary to manufacture large quantities of sulfuric acid. Lead was naturally adopted for construction, and, although its strength was decidedly deficient, it was much more resistant to corrosion than iron, and gradually assumed its place as "the acid-resistant metal."

These two metals were used for many decades before research and experimentation indicated that better metals and alloys could be used for acid resistant work. In the latter part of the nineteenth century the quest for new materials of construction began in earnest, owing to the great commercial development of the chemical industries during that period. Various brasses and bronzes were used for small parts, and copper and silver were used extensively in apparatus for the manufacture of dye intermediates, dye products and pharmaceuticals. Nevertheless, the higher cost of the latter metals restricted their use to a large extent, and iron, steel and lead still remained as the principal materials of construction.

Shortly before the recent war broke out, the manufacture of special alloys for resistance to high temperatures and chemically

corrosive conditions had gained a solid footing and the rapid progress which was made during war times has entirely changed not only the complexion of the field of structural materials, but also the attitude of the engineer in his selection of these materials. There are alloys available at prices ranging from 20 cents to $10.00 per lb. They range from simple binary alloys to complex mixtures containing as many as twelve different metals. The engineer must now govern his selection of materials not on the initial cost, but he must give consideration to the following points:

1. What is the service-life of the metal or alloy under given conditions?
2. How does the depreciation cost compare with the initial cost?
3. Can parts be replaced without long delays?
4. Will the metal or alloy have a harmful effect upon the materials being manufactured?

Aside from the alloys, it should be mentioned that the pure metals are being used to a large extent under conditions where they are peculiarly fitted to resist a certain corrosive agent. The more important of these are copper, aluminum and nickel. Recent developments in the metallurgy and working of refined aluminum and nickel have made them promising competitors of some of the alloys and, in certain cases, of enamelled ware.

## Selection of Materials for Specific Corrosive Conditions

The engineer who is about to select the various materials with which to construct a plant must not only consider the initial cost of the material but must consider the rate of corrosion as well. The ultimate aim is to obtain from a material the maximum service per dollar expended and this resolves itself into determining the cost per time-unit of service. Where a cheap material which corrodes more or less readily is selected, the products of corrosion must not be objectionable in the product which is being manufactured. The replacement and repair costs must also be considered when selecting a material of this sort. The advantage usually lies, however, with the material which does not corrode so quickly and which costs more. The installation is more permanent; the chances of contaminating the manufactured product are not so great; and the replacement costs are lower.

The following list of materials which are resistant to specific corrosive conditions, has been compiled principally from the records of the duPont Co. Many arbitrary tests were made upon various materials at the several plants and, where valuable conclusions could be drawn from the results, they have been included here. The larger portion of conclusions have been drawn from standard corrosion tests which were performed by the Jackson Laboratory of the duPont Co. It may be well to say here that these conclusions have taken material cost into consideration in some cases but since the resistance to corrosion is the more difficult to determine, it has been considered alone in the majority of instances.

Several of the relatively new acid-resisting alloys which have appeared on the market, and for which merit is claimed, have not yet been tested and cannot, therefore, be rated in comparison with materials whose resistance to corrosion is already known for specific conditions.

It should be kept in mind that prospective apparatus should be designed wherever possible from the same material or, at least, the same material should be used in all parts of the equipment which are exposed to corrosive conditions. Where two varieties of iron or steel are to be used and a certain amount of electrolytic corrosion is expected, the metals should be tested for polarity while exposed to the corrosive reagent in order that the electronegative variety may be used for the container. Observance of this detail is not of great importance when dealing with cast iron and steel since practice has already determined the proper disposal of these metals, but where the equipment is to be of "all steel" or steel and wrought iron, a preliminary test for polarity and potential difference is occasionally a good investment where unusual corrosive mixtures are to be handled.

## Acids

*Acetic Acid.*—Aluminum is gradually replacing copper in the construction of apparatus for acetic acid work. Copper still remains the most desirable material for use in the distillation of crude acetic acid owing to the presence of formic acid which has a very destructive action on aluminum. The presence of even ½ of 1 per cent of formic acid in crude acetic acid from acetate of lime will destroy aluminum equipment in a very short time. The

lower concentrations of pure acetic acid—i.e. from 1 per cent to 10 per cent—do slightly corrode aluminum but this is usually not considered serious enough to prevent its use. Acetic acid from an aluminum still is uncontaminated with metallic impurities even when air is present in the still. Copper gives satisfactory service only after all air has been washed from the system. The distillate is colored with copper salts and must usually be re-distilled. If precautions are not taken to prevent the surging of air in and out of the copper vent, this portion will also corrode.

Aluminum is therefore recommended for the concentration of pure acetic acid, separation of acetic from the higher homologues, and for condensing and cooling coils when the cooling water is neutral to litmus. Slightly alkaline cooling water tends to cause a pitting action which will destroy an aluminum coil within a very few weeks.

Duriron resists the corrosive action of acetic acid very well. It is rarely recommended for this work, however, since the apparatus is unwieldy, liable to fracture and possesses but little intrinsic value.

Nickel has given satisfactory service with acetic acid but has been restricted in use during the past, owing to the fact that it could be obtained only in the cast form. The castings were usually very porous. Now that nickel may be fabricated in the same manner as copper or sheet steel, it will undoubtedly be given serious consideration along with aluminum and copper.

Silver is occasionally used for containers and for condensing coils in acetylation and acetic acid reactions, particularly those for the production of fine chemicals in which contamination must be avoided.

The following materials are to be recommended for use with acetic acid. (1) For storage of weak acid—up to 10 per cent concentration—wood or hard rubber lined tanks should be used for large quantities. Earthenware or glass may be used for small containers. (2) For commercial acetic acid (containing a small percentage of formic acid), wood for storage, copper for reaction vessels and hard rubber or copper alloys for pumps, containers or carriers. In the latter case, the copper will be slightly attacked by the acid and where necessary, the color may be removed by precipitation with potassium or sodium ferrocyanide. (3) For glacial acetic acid reaction vessels, aluminum, nickel, copper and lead, respectively, aluminum being most resistant, and for pumps, storage and carriers, aluminum or hard rubber. The use of wood is both

expensive and unsatisfactory when used as carriers, since the wood not only imparts an objectionable color to the glacial acid but the latter causes the wood to shrink and deteriorate with the result that leakage soon occurs. Experience has shown that the cost of frequent replacement and leakage losses outweighs the cheapness of wood as a material for containers, and the present tendency is undoubtedly toward the use of aluminum or hard rubber-lined carriers for inter-plant and intra-plant shipments. (4) Aluminum should be used for acetic anhydride containers, although steel is generally used for this purpose. Serious leakage losses have been experienced with steel, however, and aluminum is considered to be safer.

*Chloracetic Acid.*—This acid readily corrodes most of the common materials of construction. Nickel has been found to stand up better than the other metals, although lead may be used in parts of chloracetic equipment.

*Fatty Acids.*—Propionic, butyric, Brown Acid, strong-after-glacial, etc., may be handled in the same materials as acetic acid, the same order in the choice of materials being observed. Formic acid is an exception to the general rule.

*Formic Acid.*—Bronze resists 85 per cent formic acid better than any metal so far tried. Copper resists this acid fairly well and much better than any of the other metals except nickel, which is said to show equal resistance with copper. Iron is readily attacked and aluminum dissolves very rapidly once the oxide coating is broken. Copper or nickel are, therefore, the metals which should be selected for this work. If riveted sheet bronze construction can be procured, it should last about twice as long as copper.

*Hydrochloric Acid* of low concentration is practically never handled in metallic equipment. Stoneware, glass, hard rubber or wood are always used, the selection depending upon the operation for which the acid is to be used. Wood is selected where large scale operations are being carried on at elevated temperatures, hard rubber is selected for piping, valves and pumps, glass being used only for pulsometer lines, and stoneware for parts of the hydrochloric acid plant itself. Special hard lead is sometimes used for reaction vessels in small scale operation.

Enamelled equipment has been, in many instances, the only resource of the chemical engineer in carrying out an operation in which hydrochloric acid was used or evolved. Experience has

shown this type of equipment to be an expensive investment and only warranted when nothing else will do.

At present, concentrated hydrochloric acid is handled in stoneware, hard rubber, glass and bitumen. Stoneware is used principally as pulsometer reservoirs and for storage of two or more carboys of acid at a time for some particular operation. Hard rubber is used for pumps, acid lines, valves fittings, etc., and for lining steel tanks and tank cars for the transportation of this acid. It should not be used, however, if the acid is likely to be contaminated with benzene, as may sometimes happen. Raw rubber is used for lining large wooden storage tubs and is known to give excellent service. Glass is used principally in the form of enamelled apparatus. Bitumen resists hydrochloric acid very well and has been used in the form of Positive Seal Cement for lining the wooden tanks of the old type hydrochloric acid tank car. Coal tar pitch appears to be almost as resistant as the asphaltic material but is not to be recommended, since it cracks and checks during cold weather and flows in warm weather. Moreover, it does not possess enough elasticity to prevent it from cracking or chipping off when suddenly stressed. Of the above materials, however, enamelled equipment is the most generally used although every effort is being made to develop a more serviceable substitute.

A special grade of Tantiron is claimed to be resistant to hydrochloric acid but tests which have been made on this alloy have shown that it has very little, if any, advantage over the ordinary grade of ferrosilicon alloys.

Hydrochloric acid vapors may be safely handled in iron if their temperature is above the dew point, otherwise, earthenware should be used. Lead is frequently employed for vapors which are allowed to escape to the open air from reaction vessels, and wood fume stacks are used to carry off hydrochloric acid vapors from wooden tubs. Dry hydrogen chloride may be handled safely in iron pipe and iron tanks and is usually stored in a gasometer in which concentrated sulfuric acid is used as the sealing liquid.

*Hydrofluoric Acid* is not used to any great extent on a large scale but it is interesting to know, however, than 60 per cent HF may be safely shipped in steel drums which have previously been passivified as described briefly below. The steel drums are filled with 58 per cent hydrofluoric acid and kept at 80° F. for 48 hours, then at 140° F. for 7 hours, allowing any gases to escape through

a ventilated bung. A protective adherent crust is formed which allows drums to be used in this service until worn out mechanically. The passivifying treatment is, of course, repeated periodically to preserve the protective coating. The same passivifying acid may be used over and over again until it has to be strengthened. These drums should be used only for shipping hydrofluoric acid and should never be washed out with water.

*Lactic Acid.*—The same general precautions should be observed in handling lactic acid as those described under acetic acid. It is perhaps more important that lactic acid be handled in aluminum than acetic, since the purer grades are used for edible purposes, and should contain no poisonous impurities. In the past, it has been standard practice to ship this acid in oak barrels, since the greater part of it was used in the tanning industry, but when the pure grade is shipped or stored, aluminum is the logical material for a container.

*Mixed Acid.*—Practically all of the useful mixed acids can be safely handled in wrought iron or mild steel. Few, if any, of them contain more than 20 per cent water and practically all of them contain 15 per cent or more of sulfuric acid. The principal danger involved in handling mixed acids is from their avidity for moisture, which brings about dilution of the films of acid in pipe lines and on the upper surfaces of storage and weigh tanks. The diluted acids destroy the container in a surprisingly short time in a manner which is called surface line attack. Every precaution should, therefore, be taken to exclude moisture, either as liquid or vapor, from the mixed acid storage system. Tanks should not be left open to the air except through a long vent and particular precautions should be exercised that all condensed water is blown out from the compressed air line before transferring acid. Mixed acids which contain 20 per cent or more of water should be stored or shipped in lead-lined tanks.

*Nitric Acid* is rarely if ever handled on a large scale, except in Duriron or glass, and to some extent in lead, for the stronger grades. Drum shipments of pure nitric acid whose concentration is 90 per cent or over may be made in aluminum. Practically all of the nitric acid used in the industries is handled in the form of mixed acid or is added to the particular operation as sodium nitrate. Duriron, glass, and earthenware equipment are used to a large extent in the manufacture and concentration of nitric acid, but in

some cases where the straight acid is required for an operation it is syphoned directly from a carboy. Enamelled ware has been used for operations where the addition of straight nitric acid was required, and although this type of equipment has given better service than any other, it was found to be susceptible to surface line attack, the points of failure appearing in every way to be due to a slow solvent action of the acid on the enamel itself. Where concentrated sulfuric acid is present, the straight nitric acid may be safely added to cast iron or steel equipment.

*Sulfuric Acid* is without doubt the most widely used acid in the chemical industry. In the various operations practically all concentrations of this acid must be handled, and consequently, the materials used in the construction of apparatus cover practically the entire field of metals, alloys, wood, glass, enamel, etc. Concentrations up to 30 per cent (cold) are handled in either lead or wood, although the use of wood for concentrations above 10–15 per cent is not considered an economical practice. Even 5 per cent sulfuric acid tends to dehydrate and shrink wood and this accounts for the constant trouble that is encountered with leaky tanks and tubs even when they have been kept well swelled with water when not in use. The only way which has been found to overcome this difficulty is to construct wooden tubs from tongued and grooved lumber. When being assembled, the dry tongues and grooves are thickly coated with some plastic composition similar to rubber cement which is relatively acid resistant. On tightening the hoops, this compound is forced into every crevice and affords an elastic cushion which offsets the shrinkage of the wood while the tub is being used in acid service. Lead is the most serviceable metal for use with sulfuric acid up to 80 per cent strength (boiling). Above 80 per cent, cast iron is the most satisfactory construction material and although the ferro-silicon alloys resist corrosion slightly better, they are not so easily adapted to complicated designs and do not stand up in active service so long as cast iron. Where the lower concentrations are to be handled and somewhat more rigid apparatus is desired than is afforded by lead, the so-called hard lead is used. Hard lead is usually slightly less resistant to sulfuric acid than pure lead but is more permanent because of its greater strength and consequently, its lesser tendency to creep and warp.

When it is desired to handle the lower concentrations of this

acid in metal equipment, a lead lining is usually resorted to. This practice, however, generally gives very poor satisfaction, owing to the exceptionally low heat transfer that is realized in jacketed equipment. For the most economical operation a lead-lined apparatus should be heated by means of an internal lead coil. Even this method is unsatisfactory in the end, however, because the coil is subject to the same drawbacks as sheet lead and in time loses its original shape and must be replaced. The anchoring of a coil of this sort presents one of two difficulties in that either a stronger and more susceptible metal, or lead must be used to support the weight of the coils. The solution of most of the above difficulties is obviously seen in the use of the so-called homogeneous lead linings. Of those which have appeared on the market from time to time, the most promising seems to be the "Zeitler" construction which has been introduced to the trade by the Oakland Copper & Brass Works of Oakland, Calif. A crimped wire screen, which has been tinned, is riveted to a tinned steel plate with copper rivets. The lead lining is then cast onto this screen in any desired thickness. The screen serves to give the lead lining a good anchorage and the tinned surfaces assure good contact and consequently optimum heat transfer, since it alloys with both the steel and the lead. This type of construction appears to have a promising future.

Cast iron is generally used for nitrators when nitrating with sodium nitrate, and although the concentration of the sulfuric acid at the start is usually from 60–65 per cent, the inner shell of the nitrator has been found to stand up in service very well when the reaction mixture was removed as soon as finished. The final acidity is usually 34–38 per cent, but this exists in the form of an almost saturated solution of sodium acid sulfate and it is believed that the large proportion of the sodium salt present tends to diminish corrosion materially.

*Sulfurous Acid* solutions readily attack most metals, so, for lower concentrations wood is used, redwood being much more preferable than the other varieties. Higher concentrations than 5 per cent of sulfurous acid, as such, are rarely used, but lead, bronze and copper are the metals that are generally employed for this work. Dry sulfur dioxide gas and dry liquid sulfur dioxide may be handled in iron or steel tanks or pipe lines.

## Alkaline Corrosive Agents

*Caustic Alkalies.*—Sodium and potassium hydroxide, or mixtures of the same, differ very little in their effect upon the metals. Of the commoner metals, those which resist caustic alkali well enough to be used for chemical apparatus are nickel, monel metal, copper, wrought iron, low silicon cast iron and mild steel, nickel being the most resistant. Nickel is widely used in the laboratory for caustic fusions but on account of its relatively high cost as compared with iron, it has not been considered for use on a large scale. Copper is not often employed because of the impurities it introduces into caustic reactions and the difficulty of their removal in ordinary operations, particularly if the caustic be used in low concentrations. Considering all factors, copper is but little better than iron or steel for reactions where the concentration of the caustic is below 37°–40° Bé., and, if the operation has not been standardized to that extent which would warrant the expenditure for riveted nickel equipment, low silicon cast iron or cast 5 per cent nickel steel should be used. Iron stands up quite satisfactorily in very dilute solutions of caustic, but the presence of the latter facilitates atmospheric corrosion somewhat.

Although strong caustic solutions are very destructive to wood, it is sometimes necessary to use it when these solutions are to be acidified and metallic impurities would be harmful to the product. In such cases, e.g., caustic fusions of certain sulfonic acids, the autoclave charge should be cooled as far as practicable before blowing to wooden tubs and neutralization should begin immediately. Whereas strong caustic solutions tend to disintegrate wood by dehydration and partial solution, the weaker solutions accomplish the same result by hydrolysis and partial solution, and for this reason lead linings are sometimes used and have been found to stand up very well in less than 10 per cent caustic solutions if the temperature is not allowed to exceed 90° C. At ordinary temperatures lead satisfactorily resists concentrations up to 25–30 per cent. Lead is susceptible to corrosion by caustic with the formation of soluble salts, but for the reaction to assume any noticeable proportions, the concentration of the caustic must be above 10–15 per cent, the temperature must be elevated, and usually an oxidizing agent must be present.

Strong caustic and soda ash solutions cause rapid deterioration of filter cloths, particularly when the latter are subjected to high temperatures for prolonged periods. It is occasionally more economical in the end to use metallic filter cloths of monel metal if the precipitate is not of a semi-colloidal nature. If the liquors contain sulfides, however, monel metal cloth should not be used. Cotton cloths are more economical for filtering dilute alkaline liquors.

*Ammonium Hydroxide.*—There are relatively few places where ammonium hydroxide, as such, is used as one of the principal components of a reaction. Its occurrence is usually incidental to a slight decomposition of amino compounds during the caustic fusion of an organic amino sulfonic acid, to the becoming alkaline of an iron reduction of a nitro hydrocarbon, or as a by-product in such operations as the following: (1) Destructive distillation of coal; (2) hydrolysis of an amino sulfonic acid by means of the sulfite ester reaction; (3) hydrolysis of amino sulfonic acids at high temperatures and pressures with dilute sulfuric acids; (4) reduction of the residual nitric acid in diluted nitration masses of naphthalene sulfonic acids, with iron, etc. In the latter two cases, the ammonia does not occur as such but combines with the excess acid. With the exception of the first case, which is one of the principal sources of supply, little effort is at present being made to recover the ammonia.

The more common cases where ammonia is used as one of the principal constituents of the reaction are: (1) manufacture of ammonium nitrate from ammonia liquors and recovered nitric acid; (2) digestion under pressure of an aromatic nitrochlor hydrocarbon with concentrated ammonia to form the corresponding nitroamino compound; and (3) the digestion under pressure with a naphthol, e.g., beta-naphthol, to form the corresponding beta-naphthylamine. In each of the three above cases, special conditions prevail which determine the nature of the equipment which may be used.

In the first case, the ammonia liquors are stored in closed steel tanks, particular attention being exercised that as few connections as possible are made above the liquid level because moist ammonia vapors have been found to be more corrosive than the liquors. During the neutralization, a brick-lined wooden tub, placed underground, is used.

The second case is typical of a condition where the nitro group acts as an oxidizing agent and corrosion takes place in spite of the exclusion of all air from the autoclave in which such a reaction is carried out. If the product which is being manufactured is of such a nature that it must be free from small traces of metallic impurities and is very difficult to purify, enamelled equipment must be used. Even the acid resistant metals are susceptible to this type of corrosion and cannot be used without contaminating the product. The same is true when purifying delicately colored products by recrystallization from ammonium hydroxide solutions. If air is present, it usually takes part in the reaction and the corrosion products which are formed result in an impure product. Thus, when dealing with these conditions, it should be remembered that products whose purity is judged by the clearness of color and which are difficult to purify, should be handled in enamelled equipment. Aluminum and tin are said to be unaffected by ammonia alone even in the presence of air, but the former cannot often be used, since the presence of only small amounts of alkali salts form alkali hydroxides and rapidly attack the metal.

The third case is typical of a reaction whereby a product is obtained that is readily purified and, in fact, must usually be purified before it can be used for subsequent operations. In this instance, iron or steel equipment give entirely satisfactory service. There being no oxidizing agent present beside air (the major part of which is washed out of the autoclave by volatilization of the ammonia) there is very little corrosion and the crude product is only slightly contaminated with iron, which remains behind in the residue when the product is sublimed or distilled.

Where ammonia is evolved as a by-product, it is usually handled in lead lines if the vapors are moist. Iron lines may be used for the dry ammonia gas, liquid ammonia and moist ammonia vapors if, in the latter case, the presence of iron rust is not objectionable in the condensate.

Copper should never be used where it will be exposed to ammonia. It is easily attacked either in the form of pure copper or its alloys.

### Salts and Other Compounds

Notwithstanding the fact that a great deal of effort has been expended on the the collection of data with regard to the corrosive

properties of neutral and other salts, there is still a great deal to be learned. Only the most pressing problems have been investigated, particularly those which involved a very appreciable corrosion rate, and those salts or compounds which do not corrode iron or lead very seriously have received but little attention. As a result, the data which follow must, in most cases, be considered as more or less arbitrary since they were sometimes gathered in hurried tests which were made more with the object of determining whether a certain metal would be satisfactory or possible, rather than which metal of those available would give the most economical service. It is quite possible that in some instances better materials may be found.

*Aluminum Chloride* is used in several condensation reactions, notably the Friedel and Craft's reaction. It is, of course, used as the anhydrous salt and, during the reaction, hydrogen chloride is evolved. If the reaction is anhydrous, as should always be the case, it may be carried out in iron or steel equipment without danger. Precautions should be exercised, however, that when running intermittently, the equipment be flushed out after the last run of a series with dry air or some anhydrous volatile solvent followed by air, in order to remove hydrogen chloride. If these precautions are not taken, the deliquescent vapors will attract moisture from the atmosphere and hydrochloric acid will condense upon the vent line and sides of the reaction vessel. A thorough cleaning will then be necessary before the next run is made in order to avoid contamination of the product with iron salts.

*Aluminum Sulfate (Alum)* tends to hydrolyse with the formation of sulfuric acid which readily attacks iron. Lead is recommended for piping and hard lead containing about 9–10 per cent of antimony is advised for rigid equipment.

*Ammonium Chloride Solutions* up to 10 per cent strength may be handled in lead.

*Ammonium Nitrate,* when dry, is stored in iron barrels. The moist salt corrodes the barrel and "sets" into a solid lump which is difficult to remove. Copper, monel metal, the brasses and bronzes should not come in contact with the salt during its manufacture or its incorporation in any of the explosives, for although the copper corrosion products are not known to form sensitive compounds with the ordinary explosives or explosive mixtures, they do tend

to lower the ignition point of such mixtures as amatol. Tin, on the other hand, is thought to form sensitive salts with ammonium nitrate and should, therefore, be avoided. Wood and aluminum are the two materials which are usually recommended for mixing ammonium nitrate with other explosive ingredients.

The evaporation of ammonium nitrate liquors at one time presented a very serious problem, owing to hydrolysis of the liquor to ammonia and nitric acid, accumulation of the latter and electrolytic corrosion between the cast iron vessel and the wrought iron steam coils. These difficulties were overcome by the use of an anti-acid to neutralize the excess acid and by thoroughly insulating the steam coils from the rest of the machine, and finally, all parts of the machine from the ground. This was accomplished by means of non-conductor gaskets and bolts equipped with mica sleeves and washers.

*Aniline and Other Amino Hydrocarbons* have a peculiar corrosive action on copper, brasses, bronzes, aluminum, magnesium (and perhaps some of the other metals) owing to the displacement of one or more hydrogen atoms in the amino group by the metal itself. This reaction is usually considered to be a high temperature reaction, although instances are known where 3 per cent solutions of aniline in hydrocarbons have readily attacked copper at ordinary temperatures.

*Antimony Chlorides* are generally used as chlorinating agents. The tri-chloride crystals are chlorinated in an enamelled or lead lined vessel and pentachloride, which is a liquid, is used in the same manner as the phosphorus chlorides. These reagents are very corrosive and have been known to attack enamelled equipment in a short time. The reactions are anhydrous and hydrogen chloride is usually evolved. Enamelled equipment is preferable on account of its cleanliness, but lead is perhaps more economical.

*Benzaldehyde* corrodes zinc noticeably. In this case an arbitrary test was made with several metals, zinc giving better results than the others. It seems probable, however, that a more useful and adaptable metal could be found if necessary.

*Benzoic Acid Vapors* corrode the commoner metals quite readily at a high temperature (250° C.). Nickel, monel metal and copper gave the most satisfactory results, nickel being best. Monel metal (hardness = 20) corrodes about 50 per cent more rapidly and

copper corrodes about three and a half times as rapidly. Preference should be given to nickel notwithstanding the cost price differential.

*Bromine,* like the other halogens, may be stored in iron when kept cool and absolutely dry. When used in chemical equipment, even when the reaction is supposedly an anhydrous one, the bromine attacks iron locally. A remedy which is frequently used to good effect is to allow the bromine to flow or react in a porcelain or enamelled dish. The hydrobromic acid which is formed will not affect the iron equipment if proper precautions are taken to keep out moisture. Enamelled equipment should always be used if the reaction is not anhydrous.

*Chlorbenzol* may be safely handled in iron containers if it has been freed from residual hydrochloric acid.

*Chlorine,* when dry and gaseous, may be handled in iron or steel equipment and conveyed in iron lines. When used in chlorinations under anhydrous conditions, it should be remembered that hydrochloric acid is evolved and should be removed between operations. Where moisture is present, enamelled or ferro silicon equipment should be used. Lead has occasionally been used for chlorination operations when a substitute for iron or steel was desired.

*Ferric Chloride* is very corrosive to iron, nickel, copper or monel metal equipment; in fact, few metals satisfactorily resist it. Enamelled apparatus is claimed to be the most economical equipment.

*Formaldehyde* may be handled in iron equipment with neither appreciable corrosion of the iron nor pollution of the formaldehyde.

*Iodine.*—The same remarks apply to iodine as those found under bromine.

*Nitro-Chlor-Benzol.*—A test has shown that brass and copper resist moist boiling mono-nitro-chlor-benzol only fairly well, although the corrosion rates are not so high as to preclude the use of these metals.

*Nitro-Phenol (Para).*—Copper resists a saturated boiling solution of p-nitro-phenol very satisfactorily. Lead indicated poor resistance.

*1:4 and 1:5 Oxy Acids.*—The conditions which arise in the manufacture of these two acids (Neville and Winther's, and Oxy L Acids, respectively) require resistance to caustic soda, sodium bisulfite, ammonia, hydrochloric acid and sulfur dioxide (moist). The only cheap metal which seemed to satisfy these conditions

fairly well was lead, although, in service, it was found to succumb rather quickly. No completely satisfactory substitute has been found as yet. The corrosive conditions are so incompatible for any one alloy or metal that perhaps the ultimate solution will be the use of two separate vessels with adequate facilities for quick transfer from one vessel to the other. One vessel would be designed to resist the acid group of conditions, and the other the caustic and ammonia group.

*Phosphorus Chlorides.*—The various chlorides of phosphorus which are used as chlorinating agents owe their reputation as extremely corrosive substances to the fact that hydrogen chloride is usually evolved during the chlorination reaction. When the conditions which surround the reaction are anhydrous, iron and steel equipment may be used with safety but it should be pointed out here that the same care and and precautions should be taken as those described under the paragraph on Aluminum Chloride. If these precautions are not taken, it will be necessary to resort to lead lined or enamelled equipment. The nature of the reaction requires that conditions be anhydrous in order to utilize all of the available phosphorus chloride but conditions sometimes arise where a small amount of moisture is present at the beginning of the reaction and in such instances hydrochloric acid is always formed by hydrolysis of the phosphorus compound. The temperature of the equipment then is the deciding factor, for if it is lower than the dewpoint corresponding to the concentration of the hydrochloric acid, active corrosion will take place. Thus, the essential consideration in deciding upon equipment to handle this type of reaction is whether or not anhydrous conditions can be maintained. If so, iron and steel equipment may be used when the proper precautions are taken. Otherwise enamel or lead lined apparatus must be resorted to.

*Polysulfide Solutions* give very little trouble and up to the present time iron equipment has given satisfactory service except for the first few runs. Iron is found in the product when making the first few fusions in a new machine, but it is believed that the formation of a protective coating of possibly some iron sulfide makes the equipment passive to further corrosion.

*Salicylic Acid.*—When moist salicylic acid vapors come in contact with iron a purple decomposition product is formed which

colors the final product and makes it unfit for the market. Tin does not seem to be affected by moist vapors.

*Sodium Bisulfate* in aqueous solution readily attacks iron. Lead lined wooden tanks are usually used to handle this material. Where the sodium bisulfate is fused and where the fused salt is used as a sulfonating agent with strong sulfuric acid in lieu of oleum, iron is a satisfactory material for equipment

*Sodium Chloride* solutions slowly attack iron, particularly when conditions are favorable for electrolysis. Lead may be used for tank linings where necessary. Copper, bronzes, brasses and monel metal all withstand boiling 10 per cent solutions of this salt satisfactorily.

*Sodium Hydrosulfite* as such in neutral solution does not corrode iron very rapidly. The use of this metal is usually proscribed, however, on account of the danger of contaminating the hydrosulfite. Both iron and aluminum are usually avoided and lead, although fairly satisfactory, is not often used for permanent installations. The metals which have been found to resist this reagent and to assure cleanliness of the product are tin, nickel and monel metal. They not only withstand corrosion by solutions and suspensions of the salt itself, but also the other reagents that are met with in the process of manufacture. This does not include, of course, the first step in the process. There seems to have been a considerable difference of opinion with regard to the material for the digestor and where enamelled equipment was actually used for this operation, it is thought that iron or steel would give equally good service, and any small amounts of iron that dissolved off would be removed during the preliminary filtration.

*Sodium Hypochlorite* solutions up to 20 per cent concentration may be safely handled in iron or steel equipment. Copper is also satisfactory. Lead is not recommended.

*Sodium Sulfate* solutions of 10 per cent concentration at the boiling temperature can be handled in iron or lead. Copper is also satisfactory. This salt has been found valuable in decreasing the corrosion of the lead linings in wooden tanks which are used to collect spent nitrating acids and wash waters. It was found that a 10 per cent salt-cake solution in the tank reduced the corrosion to a little over 3 per cent of the former rate in one case tested. The spent acid in this case contained about 4 per cent $HNO_3$ and 2 per cent $H_2SO_4$.

*Sodium Sulfide* solutions corrode iron only very slowly and it may be said that the atmospheric influences here are more effective than those exerted by the sodium sulfide. Where an iron-free product is desired, it is not necessary to avoid iron equipment but frequently to remove rust from equipment which has been standing idle, before using it. Monel metal is particularly susceptible to sulfides and should not be used as tank linings or as metallic filter cloth where solutions will come in contact with it. Lead resists sodium sulfide solutions fairly well.

*Sodium Sulfite* is not usually handled in iron or steel. Solutions up to 20 per cent concentration at 25° C. may be handled in lead and monel metal. Redwood has also been found to resist solutions of this salt satisfactorily.

*Sodium Thiosulfate.*—A test has shown that mone[1] metal resists a 10 per cent solution of this salt at 80° C.

*Superheated or High Pressure Steam.*—Iron valves are not recommended for permanent installations, owing to the susceptibility to corrosion at the high temperatures involved. Brasses and the ordinary bronzes are not suitable on account of the tendency of the valve disks or gates to warp. Experience has shown that nickel and nickel alloys withstand the corrosive and erosive conditions of high temperature steam much better than any other common metal or alloy, and moreover, are not subject to warping. For these reasons, the disks, gates, valve seats and sometimes the whole valve is constructed of nickel or some high nickel alloy, such as Aterite, monel metal, etc.

## Special Metals and Equipment

Special alloys and equipment have appeared in the chemical equipment field from time to time and it is often difficult to determine whether the optimistic claims which are made for these materials will be fulfilled in actual practice. In the majority of cases, manufacturers give service as well as sell material and they generally advise against the use of their material if they believe the results to be obtained with it are open to question. Notwithstanding this, it is frequently a difficult problem to decide whether an advantage is to be gained in the adoption of highly corrosion-resistant equipment at high cost or in the adoption of less resistant equipment at the usual cost.

Six factors stand out above others in making the decision. They are: (1) Permanence of the process; (2) Long life of equipment, or in other words, cost per unit of time while equipment is in service; (3) Contamination of manufactured product with products of corrosion; (4) Replacement cost including replacement repairs, as well as time and profits lost by shut-down; (5) Efficiency of machine with respect to heat transfer, etc.; and (6) Intrinsic value of structural materials when the equipment is scrapped. They should all be given consideration, particularly if the equipment is not to be temporary.

*Alloy Steels* are often used as corrosion resistant materials in the chemical industry. The use of stainless steel, which is an 11–14 per cent chromium steel, is limited to cutlery, surgical instruments and sheets for lining equipment used in the manufacture of fruit juices. Some of the claims made for this alloy have been misleading, for, although the metal resists atmospheric corrosion even at moderately high temperatures, as well as attack by acid fruit juices, it is susceptible to attack by mineral acids and under certain conditions corrodes almost as readily as steel. It is of interest to know that when rust once begins to form on stainless steel and is not removed, the alloy corrodes in the atmosphere much the same as does ordinary steel.

*Nickel Steels* are of interest for two reasons. Caustic fusions at high temperatures are known to cause embrittlement of ordinary steel and experience seems to have shown that addition of 5 per cent nickel to the steel tends to prevent this difficulty. The second valuable use for nickel steel is based upon the discovery of Guillaume in 1898. He found that the addition of nickel to steel had a profound effect upon its coefficient of expansion. When steel contains 23–24 per cent nickel the coefficient of expansion is almost twice that of ordinary steel. With 36–37 per cent nickel the coefficient of expansion is almost zero. The latter alloy called "Invar" is used for clock pendulums, hair springs, balance wheels for watches, measuring tapes for surveying, etc. As the percentage of nickel is increased, the coefficient rises again and at 42–46 per cent nickel a series of alloys is obtained whose expansion coefficients are very nearly the same as that of glass. These alloys are called "Platinites" and have been used as lead wires through the glass stems of electric light bulbs, wire screen for reenforced

window glass, etc. It is thought that such alloys should find use also as a base metal for enamelled equipment for, by this means the destruction of the enamel coat due to thermal expansion is avoided.

*Monel Metal* gives satisfactory service in contact with fused caustic soda. It cannot be recommended for use with either gaseous hydrochloric acid or its water solutions although at ordinary temperatures, dilute acid up to 2 per cent does not seem to appreciably attack this alloy and when cold, even 10 per cent HCl may be handled. Lack of experience with this material on a large scale naturally forbids definite recommendations in connection with HCl, the above data having been obtained in connection with laboratory tests. These tests have shown monel metal to be slightly attacked by formic acid but not affected by palmitic, butyric, or oleic acids. It is said to be resistant to benzoic, carbolic, citric, lactic, cold picric, salicylic, tannic and hydrocyanic acids. Chlorine has little or no effect upon this alloy. It is only slightly attacked in cold electrolyte solutions although it is not recommended in contact with other metals and an electrolyte solution. Such a combination, however, was used with success at a dye plant where monel metal set screws were used to fasten cast iron paddles on a steel shaft. There was a potential difference of 300 millivolts under conditions of the reaction, the monel metal being electro-positive. Notwithstanding the fact that the reaction was slightly acid and the temperature 100° C., no noticeable corrosion was observed.

Monel metal can be used satisfactorily in contact with hydrosulfite and the mother liquors met with in that process but tin is preferred on account of the lower cost. It stands up well in boiling 10 per cent NaCl solution, 10 per cent sodium thiosulfate solution at 80° and most concentrations of sulfuric acid up to 50 per cent at 60° C. Boiling 1 per cent to 2 per cent $H_2SO_4$ should not be handled in this alloy although moderate concentrations may be safely handled up to 60–80° C. Monel metal is not often used with sulfuric acid but when it is desirable to prevent appreciable amounts of metallic impurities from contaminating a product, it is sometimes preferred to lead. In connection with acetic acid work, cheaper metals that give more satisfactory results over wider ranges of temperature and concentration usually exclude monel metal from consideration.

*Hard Leads.*—Three different types of hard leads have appeared

on the market and only one of these, namely antimonial lead, has been a commercial success. An alloy known as Ulco lead composed of about 98 per cent lead and about 2 per cent of calcium or barium was used for a short time. While it had the hardness of antimonial lead, experience showed that the latter was preferable for most uses.

Lead-nickel alloys were not a success owing principally to foundry difficulties. The nickel did not contribute to the alloy sufficient tensile strength to allow it to compete with antimonial leads already on the market. Their resistance to corrosion is, however, greater than that shown by antimonial leads or pure lead.

The lead antimony alloys usually contain from 10–25 per cent of antimony, although that used in the chemical industries usually contains 12–13 per cent. The eutectic alloy contains 12.5 per cent of antimony. It is soft and workable, and yet has a tensile strength about three times that of pure lead. Alloys containing more than 13 per cent of antimony contain small hard grains of metallic Sb, which tend to float to the surface if the casting is cooled too slowly. These alloys are almost as resistant as lead to sulfuric acid in the cold, but are much more easily attacked by the concentrated acid at higher temperatures. They stand up well in cold hydrochloric acid at any concentration and at 100° C. up to about 18 per cent concentration without an appreciable loss. These alloys may be threaded, but with 13 per cent antimony they are easily stripped. Where threaded hard lead is desired, an 18–20 per cent alloy is used.

*Copper-Zinc-Nickel Alloys.*—Certain of these alloys possess very satisfactory corrosion resistance and may be classed as competitors of Monel metal when their applications are taken into consideration. The two most widely advertised of these alloys are Aterite and Meco metal, manufactured by the H. M. Aterite Co.,of New York and the Midwest Engine Co., of Indianapolis, respectively. Both of these alloys are variable in composition since they are designed for use under several different corrosive conditions. An analysis of one sample of Aterite indicated the following composition: Copper 60.6 per cent, zinc 27.3 per cent, nickel 10.8 per cent, antimony 0.4 per cent and undetermined 0.9 per cent. Meco metal is composed of approximately 50 per cent copper, 25 per cent nickel, 20 per cent zinc and 5 per cent of other metals.

These alloys are not quite so resistant to dilute HCl at low temperatures as Monel metal but are more resistant at elevated temperatures. Aterite is recommended by its manufacturers for use with superheated steam, hydrofluoric and the organic acids as well as sulfuric and sulfurous acids. It is also recommended by them for calcium hydrate, caustic soda and potash. The Aterite Co. does not recommend it for chromic, hydrochloric or nitric acids, picric acid, mixed acids or ammonium hydroxide. Meco metal is marketed at present only in the form of machinery, principally pumps for handling mine waters of 0.5 to 10 per cent acidity. Laboratory tests have indicated that there are several conditions under which Meco metal would give satisfactory service in the organic chemical industry. None of these applications has so far been given a thorough try-out under works conditions, however.

*Miscellaneous Alloys.*—Other alloys which have been recommended at one time or another for chemical construction are: Ceco, Hardite, Illium, Ampco, Stellite, Bario and Magnalium.

*Ceco* is composed principally of aluminum which is alloyed with 2–4 per cent of rare earth metals and is used as a substitute for aluminum construction. The manufacturer recommends this alloy for use in connection with acetic and nitric acids, but tests which the duPont Co. has made both in the laboratory and plant indicated that aluminum resists these acids better than the alloy. Ceco alloy probably has the advantage when construction of a pump is being considered owing to its better mechanical properties.

*Hardite* which was found by analysis to be composed of nickel 45 per cent, chromium 15 per cent, iron 13 per cent, silicon 10.6 per cent, copper 6 per cent, zirconium 4 per cent, molybdenum 3.45 per cent, manganese 2 per cent, and aluminum 0.95 per cent, was first introduced as a nitric acid resistant metal. Corrosion tests showed, however, that although this alloy is resistant to 30 per cent $HNO_3$ at room temperature or 10 per cent $HNO_3$ at 55–65° C. its range of usefulness was not wide enough and its susceptibility at other temperatures and acid concentrations precluded its use for general nitric acid use. Its cost in 1918 was quoted at $3.50 per pound, rather high for a structural material.

*Illium* is an alloy which Dr. S. W. Parr of the University of Illinois developed for use in his bomb calorimeter. It is essentially a nickel-chromium alloy and has the following composition: nickel

60.65 per cent, chromium 21.07 per cent, copper 6.42 per cent, molybdenum 4.67 per cent, tungsten 2.13 per cent, aluminum 1.09 per cent, silicon 1.04 per cent, manganese 0.98 per cent and iron 0.76 per cent; total 98.81 per cent. It is claimed to be very resistant to mineral acids but especially resistant to dilute nitric and sulfuric acids. It also gives good service when used for alkaline fusions with sodium peroxide and sodium hydroxide. Illium G of approximately the above composition costs $4.00 per pound. A second illium alloy, Illium B, consisting of 50 per cent Illium G and 50 per cent iron costs $3.50 per pound.

*Ampco,* which is one of the aluminum bronzes, is composed of 85.5–87.0 per cent copper, 9.7–10.9 per cent aluminum and 3.1–3.6 per cent iron and is comparable to steel in its general properties. It is a good bearing metal and like most aluminum bronzes of approximately the above composition is claimed to satisfactorily resist acetic, lactic, phosphoric and tartaric acids very well up to 50 per cent concentration at 90° C. It resists sulfuric acid up to 50 per cent in the cold very well but 35 per cent acid at 90° C. shows a slight tendency to react. Nitric and hydrochloric acids readily attack Ampco. The duPont Co. has had no experience with this alloy.

*Stellite* is an alloy which has become better known as a material for high speed tool steels and cutlery than as an acid resisting alloy. It is composed of approximately 75 per cent cobalt, 16.5 per cent chromium, 3–4 per cent silicon, 1–2 per cent carbon, 2 per cent iron and 1 per cent nickel. 5–10 per cent of tungsten is added when the alloy is to be used as a high speed tool steel. The cost of cobalt makes the price of this alloy too high to allow of its consideration as an acid resistant alloy.

*Bario* was first introduced as a platinum substitute for laboratory ware. Its composition varies but it is approximately 85.33 per cent nickel, 9 per cent tin, 4.25 per cent chromium, 1.22 per cent tungsten and 0.2 per cent silicon. Very elaborate claims were made for this alloy and but few were substantiated by actual test. Later samples were found to contain more iron than nickel although the cost was stated at $10.00 per pound. It has neither been used nor recommended for any of the duPont Co.'s work.

*Magnalium* and *Elektron* are very similar in composition. The former is composed of about 90.6 per cent magnesium, 9.3 per cent

aluminum and a trace of iron. The latter is imported from Germany and consists of approximately 85 per cent magnesium and 15 per cent aluminum. Their specific gravities are about two thirds that of aluminum. They are of use principally for the construction of very light machine parts that are not likely to be exposed to corrosive conditions. The mechanical properties of these alloys compare very favorably with steel in some respects.

*Nickel* is now obtainable in sheets and plates so that equipment may now be constructed similar to that of riveted steel. There is a promising future ahead of nickel in the chemical equipment field. The structural strength of nickel is said to be about 3½ times that of copper and about the same as that of steel. The intrinsic value of the worn out machine after a long life is high enough to finance an appreciable portion of the replacement cost. The future of nickel seems to lie, however, in the fabricated equipment field rather than in nickel castings, because of the practical impossibility of producing large castings which are non-porous.

*Aluminum* is the strongest metal compared with its weight in use to-day if we except the magnesium-aluminum alloys which are not applicable to chemical construction. It is of most use to the chemical industry in its purest form, since it seems to be least affected by corrosive agents when pure. It is used rather widely in the food and drug product industries as its oxide is colorless and non-poisonous. Owing to the porous and open-grained structure of its castings, it is of most use in the fabricated form.

Aluminum is recommended for acetic acid equipment except when used in connection with the crude acid containing formic acid. The pure metal resists high concentrations of nitric acid and its fumes very well, but when so used the temperature should not be allowed to rise appreciably.

When handling nitric acid solutions in aluminum it is important that they be free from $H_2SO_4$, HCl and $NO_2$.

All alkalis attack aluminum readily even at low temperatures. Ammonium hydroxide does not when pure. The presence of an alkali salt, however, would preclude aluminum from consideration owing to the formation of an alkali hydroxide. When used as cooling or condenser coils attention should be given to the cooling water. If it is alkaline, it will pit and destroy the coils in a very few weeks.

All fatty acids except formic may be safely handled in aluminum, as may also phenol, cresol, alpha and beta naphthol, as well as the aliphatic and aromatic alcohols, but it should be remembered that anhydrous substances usually have a deleterious effect, particularly in the case of phenolic and alcoholic products. Seligman and Williams [1] state that only a small amount of water—as little as 0.04 per cent in some cases—inhibits the corrosive action entirely.

Amino hydrocarbons such as aniline, toluidine, naphthylamine, etc., react with aluminum in the same manner as they do with copper. These reactions are described under German Patent No. 287,601.[2]

Care should be taken that broken thermometers or mercury be kept away from aluminum equipment because mercury initiates a very strong pitting action locally.

*Heat-Resisting Alloys.*—The better known alloys which are used for heat-resisting purposes are: Nichrome, Q-alloy, Pyroloy and Thermalloy. It is, however, inadvisable to recommend any one heat-resisting alloy as a panacea for all heat corrosion ailments. Mr. Frank A. Fahrenwald, who has given considerable study to this field, has very ably presented the considerations involved.[3] The du-Pont Co. has tested many of these alloys and has found one to be superior in one installation and another elsewhere. The conditions surrounding the various experiments are, however, too involved to allow of their discussion here. Actual tests of the various heat-resisting alloys should be made under operating conditions, giving attention to their mechanical as well as their corrosion-resisting properties.

*Enamelled Equipment* has never been able to banish the feeling among chemical engineers that it is an unwelcome stranger but one whom we must recognize when necessary. This type of equipment combines the strength of iron or steel with the acid-resistant qualities of glass, but even so, the shortcomings of this type of equipment outweigh its advantages. It is fragile when subjected to stress, is relatively easily chipped when subjected to rigorous temperature or pressure conditions, the initial cost is high, the length of service is always uncertain and unfortunately the slightest break

[1] J. Soc. Chem. Ind., 37, 159T (1918).
[2] Friedlander, 12, 123.
[3] Chem. Met. Eng. 28, 680 (1923).

in the enamel coating destroys the value of the whole equipment for the particular purpose for which it is being used.

No method of applying the enamel coating will allow it to withstand the shock of a dropped monkey-wrench or other tool. Improvement is possible, however, both in the manufacture and use of this equipment. A good many of us have seen the effects of high pressure and high temperature operation on enamelled equipment and I believe we will agree that the use of an insert is generally advisable for this type of service. By this means the pressure is the same on both the inside and outside of the enamelled container, it being transmitted by means of the fusible alloy bath which is generally used. The temperature differential between coefficients of expansion of the enamel coating and the base metal is our most important difficulty. So far, correction of this difficulty has been attempted by adjusting the coefficient of expansion of the enamel to the iron with possibly some sacrifice in its quality. The more logical method of adapting this type of equipment to the rigorous requirements of the chemical industry would seem to be just the opposite. Undoubtedly, the cost would be increased by using a base metal composition similar to Platinite—previously described under Nickel—but we could determine the enamel composition which is most resistant and then adapt the base metal of the insert to conform with the required expansion coefficient of the enamel.

Enamelled equipment is generally used in connection with reactions evolving hydrogen chloride in the presence of water or water vapor. Other corrosive reactions such as chlorinations, brominations, alkylations, condensations with phosgene, aluminum chloride, and phosphorus chlorides must usually be handled in enamelled ware. This equipment is also used when it is necessary to nitrate directly with dilute nitric acid or when light-colored products are being purified by re-crystallization. It has gained favor with the manufacturers of food and dairy products, for, although there are metals and alloys which do not corrode under conditions existing in these industries, they occasionally give to these products undesirable metallic flavors. This is particularly true in the dairy industry.

*Rubber* has achieved recognition as a valuable structural material both in the hard and soft form. Hard rubber possesses excellent resistance to all concentrations of hydrochloric acid as well as equivalent concentrations of sulfuric acid. This material is, how-

ever, restricted to use at temperatures usually below 50° C. It is now made in the form of pumps, piping, pipe fittings, cocks, etc., and usually gives good service if it is restricted to those uses for which it is intended. One disadvantage which this material has, is the similarity in its appearance to iron. Repairmen have often mistaken it for iron and have seriously damaged it by applying a wrench before they discovered their mistake. The manufacturers have realized this difficulty but claim that they cannot give their goods a distinctive color without impairing its quality.

Hard rubber is used principally for storage, transportation and pumping of hydrochloric acid. It gives quite satisfactory service, too, with cold acetic acid of all concentrations. However, reports have been received that glacial acetic acid tends to alter the hard rubber and cause leakage at wearing surfaces. Nevertheless, a reciprocal pump used in this service for over three years seemed to show no ill effects.

Hard rubber fittings are of great value in installations where more than one metal is used in construction. If iron and copper or aluminum and copper lines have to be connected to the same equipment, hard rubber fittings effectually prevent electrolytic corrosion.

Benzol, chlorbenzol, phenol and similar products should not be allowed to come in contact with hard rubber equipment nor should nitric acid and the higher concentrations of sulfuric acid.

A new application of this material is its use as a lining in tanks and tank cars. The American Hard Rubber Co. have installed several of these linings during the past two years.

The principal use for raw rubber is to be found in the lining of wooden tanks for the storage of hydrochloric acid. The Goodrich Rubber Co. has usually made these installations because of special precautions which have to be taken. A tank lining of this type was installed for the Grasselli Chemical Co. in 1900 and at last reports was still in service. A recent examination showed that vulcanization had progressed only half way through the layer of raw rubber.

*Lead Linings.*—Occasionally it is necessary to resort to a lead lining in cast iron or steel equipment. Since there are very few processes, however, in which heat transfer is not an important factor, attention should be called to the sacrifice in efficiency that is involved in the use of such an installation. The low price of

lead always argues in its favor and one is often prone to neglect considering the cost of operation or cost of inefficiency involved in its use. The principal apparent cost is in its installation. It is practically impossible to overcome one objectionable feature of the ordinary lead lining, namely, the very thin layer of air between the lead lining and the container. This layer of air has been known to reduce the effective heat transfer of a steam-jacketed container at 100° C. to as low as 1 per cent of its normal efficiency without the lining. It is difficult to translate this loss of efficiency into dollars and cents, but nevertheless this factor is worthy of more than passing thought. The Zeitler construction, described in another part of this paper, seems to overcome the difficulty by assuring continuous metallic contact of the lining with the container wall.

## Conclusion

The field covered in this paper is a very broad one and consequently only the more important subjects have been touched upon. Even some of these have had to be briefly treated. The limitations of iron and steel are fairly well known. Copper, tin, zinc and some of the precious metals have valuable applications as have also metallic protective coatings, wood, brick, cement, fusible alloys, paints and varnishes. Each of these subjects could furnish interesting material enough for a paper in itself. The value of such conclusions as have been given here is largely due to a standard method of determining the relative suitability of materials and, in case of metals and alloys, a standard method of corrosion. Certainly, we should all be grateful to the duPont Co. for their unselfishness in allowing their data to be published.

In conclusion, it may be timely to call attention to the fact that a high initial cost of equipment negatively accelerates the cupidity (and oftentimes good judgment) of the purchaser and for this reason, more than any other, we do not possess the abundant data and experience which might otherwise convince us of the greater ultimate economy of the more corrosion-resistant equipment.

The material which is selected for equipment may oftentimes determine whether a process will be a success or a failure and I believe that we may consider it to be a sign of progress on the part of chemical engineers that they are showing more interest in the suitability of materials of construction and thereby combining better methods with economic costs.

## "Laboratory Corrosion Tests"—W. S. Calcott and J. C. Whetzel

### Discussion

Dr. N. K. Chaney: In the case of the dry battery business we have a very specialized case of chemical corrosion—that is, the so-called local action of the electrolyte upon the zinc container. This has necessitated the development of very precise and elaborate methods for quantitatively determining the rates of this corrosion or "shelf action" under various conditions and with various materials. One of the greatest difficulties encountered in such laboratory methods is the evaluation of uneven corrosion or pitting. If the corrosion is fairly uniform, the weight loss is a satisfactory measure; but if the corrosion is local and uneven, its effects are much more serious than the weight losses indicate. I wonder whether there are suggestions as to the proper weighting of irregular corrosion losses in the investigations carried on by the authors of the present paper.

Dr. Jerome Alexander: The point just brought up by the last speaker prompts me also to ask this question: What effect upon the corrosion of metal may be traced to the preëxisting presence of a small amount of impurities in those metals? And, second, what effect has the heat treatment, especially the speed of chilling, which affects the surface of the metal? I don't know whether you have investigated these questions or not.

Mr. A. E. Marshall: Mr. Calcott made reference to the necessity of giving preliminary treatment to metals before recording corrosion tests. A short prior treatment is also necessary in the case of non-metals. For instance, in determining the corrosion of Pyrex, or any type of glass, it is necessary to follow this procedure, because you get a temporary initial solution rate of 300 to 400 per cent of "normal." It is also true in the case of fused silica. We made tests some few years ago, and found a higher initial solution rate, which disappeared at the end of a few hours. If the figures were taken for the initial rate, they would be entirely misleading and not at all true.

Mr. Emerson P. Poste: Mr. Chairman, the point just brought out has a very interesting parallel in the action of acids on enamels.

The Bureau of Standards found that certain enamels showed an initial loss of gloss on one-hour test with practically no greater action on 1,000 hours' test.

I should like to ask the author of this paper as to the method used by him to determine the resistance of enamels. The American Ceramic Society has a committee working on the determination of the acid resistance of enamels and we should greatly appreciate information on this point.

Dr. Charles F. Hollander: I should like to ask the author of this paper how he determines the thickness of the materials after grinding "out" the pitted part of the alloyed material? Do you make the surface plane?

Dr. W. S. Calcott: We use a rectangular specimen of definite dimensions, approximately the same size in all cases; a comparatively thin specimen, so that we can ignore edge pitting. We then reweigh the metal and calculate the equivalent thickness of the metal removed. Does that answer your question?

Dr. Hollander: Do you mean the average thickness of the specimen after grinding off the pitting?

Dr. Calcott: No; we do not actually measure the thickness of the specimen at all, but simply weigh it and determine its dimensions with the micrometer, and from these determine its area. Then if it is pitted, we grind it down until the pits disappear.

The development of pitting in the metal can not be ignored and this factor must be included in the results. To determine the magnitude of the effect, we grind down on a metallographic grinding set until all the pits have just disappeared and until solid metal is reached. The loss in weight during this grinding is determined, and we can then calculate the effect of the pitting.

Regarding the first point, we consider that a pit one-eighth of an inch deep is just as bad as if the metal had been all eaten away one-eighth of an inch, because the metal is no stronger than its weakest point. Therefore we grind out the pits to reduce its thickness to the depth of the deepest pit. If there is a pinhole in it, it is just as bad for use in manufacture as if the whole of it was gone.

On the question of impurities and heat treatment, we have not studied heat treatment. We found very remarkable effects due to the presence of small amounts of impurities. In one case the presence of 0.01 per cent hydrochloric acid in a certain solution pro-

foundly altered its action on an aluminum surface; without the hydrochloric acid it resisted well, but in its presence deteriorated rapidly. For this reason plant solutions of indefinite composition are frequently used in making our tests.

In regard to testing enamel, we have had occasion to do this very seldom, and simply obtained small enamel-lined cups and carried out the tests, except that we conducted the tests during a much longer duration of time, sometimes as long as a month instead of the ninety-six hours usual. This was done because we thought that in this case there might be considerable difference between the initial and steady rates of corrosion, due to a change in the character of the exposed surface.

DR. JEROME ALEXANDER: I think the suggestion of the speaker about the effect of impurities acting on the metal is very valuable. A few years ago there was a paper published in the Journal of the Society of Chemical Industry which reported that organic acids, when very dry, will attack metals seriously. Thus, very dry acetic and lactic acids attack aluminum. But the point that I want to get at is, what was the effect of small quantities of *impurities in the metal itself*, and not in the solution that acts on the metal. How do the impurities in the metals themselves affect its attack by the various solutions?

DR. CALCOTT: We have not studied that particular point to any great extent in this particular investigation, but our experience in this particular case indicated that there was only two-tenths of a per cent of impurity in the aluminum with which we were dealing. Slight variation in the quantitative and qualitative characteristics fundamentally affect the aluminum.

DR. ALEXANDER: I wondered if things like that did not account for the effect on metals. Very slight traces of impurities may be present and the results, or some of them, may not be due to experimental errors as much as to the fundamental fact that impurities are responsible for those errors.

DR. JOHN C. OLSEN: I want to ask Dr. Calcott with relation to the surface film which is removed after a short time—whether that surface film is chemically different from the rest of the metal, or is physically different or electro-chemically different, or whether he has any idea as to what that surface film is?

DR. CALCOTT: We have very little idea. In some cases we have

found definitely that it was chemical. In the case of iron there is sometimes a small amount of iron oxide on the surface. In steel it is sometimes due to the working of the steel which has left surface layers which are electro-positive to the body of the steel. In the case I had in mind it was aluminum, which has a surface film of oxide, so we concluded that the surface film might be due to any one of these causes. But there is nearly always a surface film of different composition from the body of the material.

Mr. P. H. Groggins: May I ask whether the corrosion during the first four hours might not be considered as the true corrosion rate, as the metal oftentimes forms a protective surface; also whether the corrosion has thus not been retarded by subjecting it to continued treatment, whereas in plant processes constant recharging and washing of apparatus eliminates this protective action?

Dr. Chaney: Some of the points raised by the preceding speakers have been covered by our own investigations on the corrosion of zinc. The same factors are present in all corrosion experiments, although their relative quantitative effects may vary widely with the alloy or metal and the conditions of test employed. For instance, as Dr. Alexander suggests, small amounts of certain impurities make large differences in corrosion. The impurities may sometimes produce their effects if in the electrolyte or corrosive solution as well as if in the metal itself.

But the most important point in developing any consistent type of corrosion test is the " preliminary treatment " of the test specimens so that a characteristic and reproducible physical surface is always presented by all test pieces undergoing direct comparison. The initial corrosion rates may be varied enormously by purely physical modifications of the surface.

It is possible so to work the surface of a metal as to cause an initial inhibition of corrosion as in pack-rolled and strip-rolled zinc. On the other hand, by sand blasting, buffing, etc., the initial rate may be unduly accelerated. In every case we have to distinguish between the initial rates (whether retarded or accelerated by the preliminary treatment) and the normal rate after corrosion has penetrated and removed the original surface film. This may be done as the authors of this paper suggest, or the surface may be artificially prepared by mechanical working, or by corrosion with acids before the regular test is commenced. For example, a simple way of removing a definite

quantity of metal from the surface without mechanical stresses being set up is to corrode the surface in a suitable acid until a definite quantity of gas (usually hydrogen) has been evolved.

In our practice the tests are continued for a sufficient time to carry the corrosion well over the initial period so that the weight losses represent the later corrosion rates to a predominating degree. Except where the nature of the corrosive medium and metal is such as to give rise to protective films, the rate of metal corrosion is usually a continually accelerating one, quite the reverse of that referred to by Mr. Marshall in the case of glasses and enamels.

PRESIDENT HOWARD: I should like to ask Mr. Calcott whether he has tried any experiments in passivifying metals? That is a subject which is increasing in importance. The Bureau of Explosives a short time ago accepted as standard practice for shipment of hydrofluoric acid metal drums which had been passivified by preliminary treatment with hydrofluoric acid. Drums, passivified in this way, are acceptable and their use is being extended—that is, steel packages in place of the old lead packages. There is another point to which I do not think there has been given much, if any, study, and that is the possibility of heat treatment to increase resistance to corrosion. Aluminum, for instance, is rapidly corroded in sea water. Heat-treated, the same aluminum is highly resistant to sea water. It seems to me that this indicates a very interesting field for experiment with other metals, to see whether other metals would not have their resistance to corrosion modified very greatly by heat treatment.

DR. POSTE: Bearing on that point, with specific reference to open-hearth steel, I have looked up several references and remember one which stated that under certain conditions overheated steel corroded 20 per cent faster than normal steel.

DR. OLSEN: The point has been brought up with reference to small impurities, and I should like to ask whether an analysis was made of the metals which are given in these tables, or whether the composition is known. I may have overlooked it, but I desire to ask whether the composition of the metals is given in the published report?

DR. CHANEY: By heating rolled zinc up to a point of rapid recrystallization and cooling, we have found that the corrosion rate in acids is reduced about one-third. Unfortunately, however, the desired mechanical properties are also destroyed, so that this has no practical significance to ordinary uses of sheet zinc.

MR. JAMES G. VAIL: I have been interested in the effect of silica in solution on some of these corrosion problems. Some of you may have seen an article by Dr. John C. Thresh, published in the Journal of the Society of Public Analysis (November and December, 1922), in which he shows that silica to the extent of one in two hundred thousand in a certain water supply would prevent the solution of lead in the pipes through which the water was delivered, and render safe an otherwise poisonous supply. Another case in which silicates are effective is to stop the corrosion of aluminum by sodium carbonate. (Seligman & Williams, Journal of Institute of Metals, *28, 297–8* (1922)). More lately there has been a piece of work done which shows that silica in hot-water supply systems added in the form of sodium silicate will prevent the continuance of corrosion already started. (C. R. Texter, American Waterworks Association, Spring Meeting, 1923.) In that case it is quite evident that there is a coating formed on the metal. In other cases it is not so evident. The effect of soluble silicates on corrosion is worthy of much more careful consideration.

MR. CHAS. WADSWORTH, 3*d:* In connection with silica as affecting corrosion, there is a patent which came out rather recently on manganese and silicon in copper alloys, the resistance being attained by putting manganese and silicon in the alloy. In this case it is the silicon which seems to act as a preventive agent, but it is suggested that the surface film, which is the important thing, may be silica.

DR. ALEXANDER: I wonder if the gentleman has considered the work of G. Tammann, of Goettingen, regarding gold alloys? He found that corrosion begins at certain percentages where apparently the gold ceases to protect, by enclosure, the weaker metal. I do not now recall the details, but it seems to me those experiments have a direct bearing on the question in hand, the production of metal films.

MR. H. H. MEYERS: I should like to ask whether the rapid rate of corrosion occurs in intermittent use of metals, or whether the rate would be the normal one?

DR. EDWARD BARTOW: Have the authors considered the physical structure of these metals? They speak of corrosion decreasing as time elapses. It is known, of course, that surfaces of crystals will corrode more rapidly along certain axes than along others. When the metal is polished certain surfaces will be exposed, but after corrosion for a while, different sides of the crystals will be exposed, and

the corrosion will be less. If this has not been considered, I think it should be.

PRESIDENT HOWARD: Mr. Calcott, will you reply to these last points?

DR. CALCOTT: I think I should like first to make clear that our idea in this whole study was not to go into the theory of corrosion so much as to select from the different materials offered on the market from which we could build apparatus, those which would be most suitable. At the time the bulk of this work was done we had no opportunity to make a microscopic study of the samples or even an analysis in many cases, which is the reason for the omission of the analyses from the report.

DR. OLSEN: Have you some?

DR. CALCOTT: We have some, but not many. Take, for instance, steel. We took the mild steel that we got and tested that.

In regard to passivity, we have passivified metals several times, usually by adding some substance that we know would form a protective coating. We found on the question of the intermittent use of the apparatus that, judging by experience, the rate on the second 48 hours was the true rate. We found that by the use of the initial rate we arrived at a very low figure, not warranted by the actual life of the apparatus. If we take the steady rating, we will arrive at a figure much nearer the correct rate, unless there are extraneous facts entering in. For instance, in the case of a metal subjected to intermittent usage, and where we know that the oxide is to be acted on and the metal is not, our figures would be almost useless. Copper, for instance, oxidizes readily, and tests of that nature would be practically worthless.

The crystal structure we have not investigated, for the reason that I gave first, that our efforts were directed primarily toward selecting material which would give the most advantageous results. We had no time nor material with which to make microscopic examinations.

DR. ROBERT T. HASLAM: Dr. Calcott has recommended the second 48 hours, whereas Dr. Chaney uses the total time from the start of the corrosion test. I think the second 48 hours is preferable, because there may be either an increase or a decrease in corrosion during the first few hours. And if you take the rate of corrosion from zero time you are averaging two factors, initial corrosion and normal corrosion. So it seems to me that the second 48 hours should

give more comparable results than the rate of corrosion as determined over entire time.

MR. JOHN P. HUBBELL: There is a slightly different type of corrosion in which the surface film is extremely important. On metals which are used to resist atmospheric corrosion, particularly zinc, a protecting film is formed. In determining the probable life of such material it is not so important to know what that film is as to know what factors will form and remove it. We have been trying to work out a scheme to accelerate atmospheric corrosion. The problem has resolved itself into a study of those atmospheric conditions which favor the formation of protective coatings and those which favor the removal of the coatings. By properly alternating these conditions we hope to develop a test whose results will be comparable with atmospheric corrosion.

DR. HOLLANDER: I want to ask Mr. Calcott if he has not found that it makes a great difference how much of the reagent acts on the surface exposed? We constructed a piece of apparatus out of mild steel, and conducted a very long series of experiments in the laboratory, testing the material for thickness before and afterward, and found absolutely no corrosion which could be detected with the micrometer. We constructed later similar apparatus to that, but very much larger, although out of exactly the same soft steel with the same welds done by the same manufacturer, and so far as we could ascertain made entirely in the same fashion as the small apparatus. In the large apparatus we found, however, a corrosion which was prohibitive, and which we could only explain in this way—that there was in the large-size apparatus a larger volume of reagent on a comparatively smaller surface. Have you standardized the volume of solvent to be taken to the unit of surface?

DR. CALCOTT: The amount of the solvent must be sufficiently great so that the strength of the solution does not vary appreciably. For the larger rates of solution we would have to use a larger amount than with low rates of corrosion. We have had some experience, however, in finding that different metals were used in the stay bolts from the other portions of the apparatus.

DR. HOLLANDER: In these cases all joints were welded by the same manufacturer, and we had every reason to believe that it would act the same on the larger one as the smaller one.

MR. POSTE: Regarding the corrosion of welds, I have in mind a

specific case in which a steel tank was made by the oxy-acetylene process, using a filler of a composition essentially that of the plate. After a short period of use the filled-in metal was eaten out in a manner suggesting cutting out with a chipping hammer. In melting the filler into place the carbon is greatly reduced. There are also structural differences between filled-in and base metal. In general the conditions are such as to render the filled-in metal electro-positive to the original plate. It therefore suffers under corrosive action, as compared with the plate.

MR. ROBERT J. MCKAY: The larger volume of corroding agent in practice, as opposed to the smaller volume in laboratory test, affects the rate of corrosion seriously, because the larger volume is capable of carrying more dissolved oxygen. The importance of the dissolved oxygen factor has perhaps not been sufficiently emphasized in this admirable paper. Except where the corroding solution contains a strong oxidizing agent, the attack is much more rapid when oxygen (or air) is present, owing to its depolarizing effect and its ability to react directly in corrosion. The volume of solution is important because oxygen is sparingly and slowly soluble. It is rapidly exhausted during corrosion and the furnishing of a constant fresh supply of air-saturated corroding solution is sure to produce maximum corrosion.

PRESIDENT HOWARD: Regarding the question of welding, that is a most important matter in steel apparatus. A good many years ago I built some steel tanks for making oleum, using acetylene welding. The tanks failed in three days, in the welds. The same tanks were then made by a Wilmington firm, the Pusey & Jones Company, by the old-fashioned welding process, which has been used for many years in making the furnaces for Scotch boilers. I understand the process consists of bringing the metal up to the welding heat by producer gas or water gas, or something of that sort, with powerful blasts on both sides, and then the joint is rolled together, and it is essentially a hammer weld. Those same tanks were put in use with exactly the same thickness in 1907, and are still absolutely intact and operating today, in the production of oleum. There was just the difference between the types of weld. The steel plate in both cases was intact. Acetylene welding is a very dangerous thing to use where there is an acid on one side and water on the other side of the joint.

This particular tank, I may say, was water-jacketed. A slight

porosity of the weld, if you have only acid on the inside, would do no harm. But in this case the slight porosity allowed the mixture of water with the oleum, the temperature was up around 140 degrees Fahrenheit and that started rapid corrosion where the acid was weak, and it went straight through.

Acetylene welding for steel pipes holding corrosive gases, like dry sulphur dioxide, will last indefinitely; but if those same joints were put under water, they might fail very quickly. The electric resistance weld seems to stand very well, about the same as the old hammer weld. But the electric arc weld is porous and should be used with a great deal of caution.

Tests made of acetylene welds are of little value because it is entirely possible to make a weld in this manner that is not porous, but it is apparently very difficult in doing large work commercially to avoid some spots that are porous. For instance, before building the tanks just referred to, small test tanks were made by acetylene welding, filled with oleum and immersed in hot water for three months. At the end of that time there was no corrosion visible and on the strength of this test the large tanks were ordered, which failed in three days.

DR. HOLLANDER: We realized that, and in many cases we specified that no calking should be done whatever. Any slight porosity found by having a pressure of air on the inside of the apparatus of fifteen or twenty pounds could be discovered by putting soap-suds solution on the outside. That shows the porosity very quickly, much better than the ordinary hydraulic test will, which does not show anything, even if you let it stand a long time.

MR. W. H. LEVERETT: In one of our plants, in a reclaiming operation, welding was called for under circumstances which indicated either acetylene or electric welding. Anticipating the danger of corrosion due to electrolysis, an attempt was made to adjust the composition of the bar used for welding, so that the resulting weld would be of the same composition as the original metal. The only result was to make the weld electro-negative with respect to the balance of the apparatus, and the sheets directly on each side of the weld were corroded through in a week, while the weld stood up like a rib.

PRESIDENT HOWARD: Is there further discussion? Dr. Calcott, do you want to make any further statement?

DR. CALCOTT: I have none to make except in reply to Mr. Mc-

Kay's point. The supply of oxygen to the metal under attack is a very important consideration, and is the reason we use, in testing, the actual solution employed on a large scale. I think the point is a good one, and should be borne in mind in all tests.

PRESIDENT HOWARD: I declare this discussion closed and we will go to the next paper.

MR. W. R. CLYMER (communicated): The matter of corrosion, being very complicated, much study is needed in any particular case to determine both the causes and the remedy. Oxy-acetylene welding is not the simple matter it is sometimes thought to be, and problems arise in connection with it that also need careful and properly directed research for their solution. It should also be remembered that in 1907 welding was in its earliest stages, and that great advances have been made since that time in both its theory and its practice.

The experience of President Howard would seem to have been with welds that were not properly made, because he speaks of the porosity of the weld. A properly made acetylene weld is absolutely impervious to the passage of any liquid or gas, and thousands of them are in use under heavy pressure of many kinds of liquids, with entire satisfaction. Dr. Poste has referred to a tank in which the filler used was as nearly as possible of the same composition as the plate. If the welding rod was originally of the same composition as the plate, it would not be so in the weld, and if, in order to allow for the alteration due to the welding, the rod were made of such a composition as would actually result in the weld being the same chemically as the plate, the chances are much in favor of bad welding. Dr. Hollander says that he has specified in many cases that no calking shall be done, and that air pressure and soap-suds were used to test the porosity. As stated before, a properly made acetylene weld will meet this test properly, and, as a matter of fact, this test is used every day in many welding shops, and has proven its value for the purpose.

Dr. Poste has stated that as a general proposition the weld is electro-positive to the plate, and Mr. Leverett found that under certain conditions the weld was electro-negative with regard to the balance of the apparatus. It would therefore seem possible, although it might be difficult, to make a weld which would be neither electro-positive nor electro-negative to the plate.

Welding is not a matter of simply melting metal, but is just as much a matter of application of scientific principles as any other

process involving metallurgical or chemical reaction, as has been shown by experience as well as theoretically. In many special cases, welding has been investigated along such lines and problems have been solved and practical results obtained, which have been commercialized with satisfactory results.

It might be remarked that a number of corrosion problems in chemical apparatus have been studied, and that, as the difficulties encountered have been entirely overcome in these cases, it does not seem unreasonable to expect that in other cases equally satisfactory results should be obtained, provided that the problems are attacked by those who are thoroughly familiar with the possibilities of welding and with the methods used in scientific research.

## "Materials of Construction for Chemical Apparatus"—Harold F. Whittaker

### Discussion

Mr. Whittaker (before presenting paper): There are two typographical corrections which I wish to make. The first, which you will find on page 22 of Mr. Calcott's paper, pertains to the formula on the middle of the page. The "2.54" should be cubed instead of squared. The final term is correct as given. And then, on the cover of the preprint of my paper, my address should have been given as "Washington, D. C.," instead of Minneapolis. My name was evidently confused with that of another man in Minneapolis.

The paper is much too long to read here, but I should like to say that the object in collecting these data was to amplify and correlate the experimental data obtained at the Jackson Laboratory of the duPont Co., and to present it in such form that valuable conclusions could be drawn from it. The essential features of the original report are embodied in this paper, and, although no claims are made regarding its completeness, it is believed that not only will interest be stimulated in this subject, but also the mental attitude of engineers in the selection of the proper structural materials may be changed somewhat. Ultimate cost of chemical equipment is an important factor to be considered before final selection is made, and it is hoped that the data presented in this paper will influence engineers to believe that the cheapest is not always the least costly.

Mr. A. E. Marshall: There are several points in Mr. Whit-

taker's paper that I should like to discuss for a moment. For example, reference is made to materials suitable for distillation of acetic acid, but no reference is made to silver. In European practice it is customary to make use of silver, and I saw a plant in 1919, built in 1904, which had run continuously for fifteen years, with the original silver coils and slate tanks for the storage of all strengths of acetic acid. The silver coils were quite thin, about one-sixteenth of an inch thickness, and they showed no deterioration in fifteen years.

Reference is also made to "a special grade of Tantiron which is claimed to be resistant to hydrochloric acid." I should like to say that from the result of our experience we are satisfied that the special grade of Tantiron is not resistant to hydrochloric acid; in fact, it is not so good as some of the other alloys.

In the case of enameled equipment a suggestion is made that it might be desirable to use a nickel steel as the metallic support for the enamel, and reference is made to the so-called Platinite alloys. While Platinite alloy has the same coefficient of expansion as glass at around 200° C., there is a considerable difference at the temperature at which the enamel would flow, so the enamel would crack off on cooling and it would be impossible to get a sound article. I am familiar with this fact because of experiments made in reinforcing glass with Platinite and other alloys. In the case of monel metal we had occasion last year to make use of this alloy in a pump designed for handling 4 per cent sulphuric acid containing impurities. The pump as originally built utilized antimonial lead parts, and in this form it failed in less than three weeks. The parts which failed were replaced with monel and the pump put back into operation. The pump has been in service about eleven months, handling the same solution, and when it was torn down about four months ago was found to be in good condition.

MR. POSTE: Inasmuch as Mr. Whittaker has referred to enameled equipment especially, I should like to make a few remarks about the paper, and in doing so I will endeavor to present the point of view of the enameling industry as a whole.

Specific reference to certain statements in the paper under discussion may serve to point out useful facts in connection with the use of enameled equipment.

In speaking of antimony chlorides as chlorinating agents, the author states that "these reagents are very corrosive and have been known to attack enameled equipment in a short time." I am not sure

as to the exact case that may have been in mind, but I do know that some equipment that has been used for this type of work has failed as a direct result of imperfections in the steel on which the enamel had been fused. The shapes were pressed containers made from inferior stock, the slag inclusions in which had been drawn out in the pressing operation and had later reacted with the enamel causing weakness therein. The point in mind is the fact that the enameler has often had difficulty in getting stock of the desired quality for certain lines of product, and in such cases field trouble has often been taken as indicating an inherent chemical weakness of the enamel as a whole when such was not the case.

A further point with reference to imperfections in base metal and defects in enamel is involved in cast-iron apparatus. A certain type of field failure originally considered as a weakness of the enamel was found to be due to porosity of casting which allowed the steam pressure in the jacket to become effective under the enamel and force it off. After considerable research an iron was produced that would not develop this porosity during the enameling operation and this type of trouble seems to be at an end.

The author suggested a certain alloy as more desirable for a base metal because of a coefficient of expansion close to that of enamel. But Mr. Marshall has suggested that such alloys are not regular in their coefficients of expansion through the range involved in the cooling of enamel. This seems to be a very important point. That the relation between the coefficient of expansion of the metal and enamel is important is recognized by the enamel technologist. But he does not think that they should be equal. Enamel is strong in compression and weak in tension. It should, therefore, be kept under compression. To that end the coefficient of expansion should be lower than that of the base metal. Too big a difference will result in difficulties, however. Further, the contraction of enamel and metal should be of the same general order throughout the range of temperatures involved in cooling from the molten condition of the enamel. In this regard the alloys suggested would seem to be wanting. I should like to ask if any actual attempt to enamel such alloys has been made or was the suggestion on a purely theoretical basis?

With further reference to the matter of coefficient of expansion, we have inherited from European investigators a set of factors to be used in computing coefficients of expansion from percentage com-

position. The Bureau of Standards has investigated this matter and found that some of these factors are incorrect. If interested in this general investigation, one will find the work reported in the Journal of the American Ceramic Society, Vol. IV, page 628.

In general, the relation of the base metal to the enamel is an important one and involves the metallurgy of the metal in its original fabrication and under the heat of the enameling furnace.

In certain cases the author has stated that nitric acid has seriously attacked enamel. I think that each of the several manufacturers puts out several different formulas, each suited to a particular type of work. In some cases mistakes have been made in testing or using relatively soft enamels under severe chemical conditions for which they were not intended. Obviously an enamel designed for the dairy industry might fail with a mineral acid. Such cases are on record and have often led to an unwarranted prejudice against the enamel. On the other hand, there are on the market enamels commercially resistant to nitric acid, as suggested in Table X of Laboratory Corrosion Tests by Calcott and Whetzel.

The manufacturers of enameled equipment are quite familiar with their product in terms of its fitness for various types of work and are very anxious that it be used under conditions of satisfactory service. The prospective user protects himself and the manufacturer alike when he accurately states the essential mechanical and chemical conditions when making an inquiry.

It is stated that no "method of applying the enamel coating will allow it to withstand the shock of a dropped monkey-wrench or other tool." It seems to the manufacturer entirely unreasonable that the user should expect enamel to withstand such carelessness as that referred to. An immense amount of enameled equipment is used in industries employing a cheaper class of labor than that usually found in a chemical plant, but cases of damage from this type of carelessness are very few.

In connection with definite chemical operations, Mr. Whittaker has suggested enameled equipment in a dozen or more cases. And he has failed to mention it in several other instances in which it has given satisfactory service. He has pointed out its various disadvantages, some of which have been covered above. He has stated that its chief use is in connection with the food industries; that in chemical operations it is only used when nothing else will do, and that "the shortcomings of this type of equipment outweigh its advantages."

The manufacturer is aware of the difficulties which have been experienced in various instances. Some of these have been incidental to the development of a new industry. Others have resulted from a lack of understanding on the part of the manufacturer of the properties of his product and the use to which it was to be put. Some have been due to a lack of proper understanding and care on the part of the user. But marked progress has been made in the methods of manufacture, and efforts for further improvement are constant; the maker knows more as to the possibilities and limitations of his product; and the user more fully appreciates the necessity for proper selection and use of the apparatus.

In view of these facts, it is evident that the advantages of this type of equipment far outweigh its shortcomings.

MR. WHITTAKER: In reply to Mr. Marshall's remark I should say that silver was overlooked. We do not claim that each one of the lists in the paper is complete, but that they indicate our own experience. In some cases references have been made to more pertinent information to be obtained through the literature. Although we knew silver was not affected by acetic acid, it was left out due to oversight, and I agree that it should be included. It would probably be better to use silver than aluminum, but at the time this paper was drawn up somewhat different economic conditions prevailed; industry was returning to a peace-time basis and, due to strict economy, the use of silver was not given much thought.

Referring to the point that he and Dr. Poste made about the base metal, the references were obtained from the work by C. E. Guillaume, Comptes Rendus, 170, 1433 (1920); 170, 1555 (1920); 171, 1039 (1920). The work was begun about 1898, and I believe interest is still active in this work. Mr. Baker and I drew up a number of curves that I think showed the coefficient of expansion of nickel steel alloys up as high as about 400 degrees Centigrade, or about 750 degrees Fahrenheit, but no data were available for such high temperatures as Dr. Poste mentioned. No direct comparison was possible therefore.

A platinite composition which would, of course, contain traces of silicon, manganese, etc., could be devised that would have a greater or lesser coefficient of expansion than the glass enamel coating. Conclusions were drawn that the proximity of these coefficients would obviate the checking and destruction of enamel equipment under the

conditions of *actual service*. Owing to lack of facilities for doing this type of work, no actual tests could be made.

Mr. Poste mentioned corrosion of enamel. I have seen an example of this in a vessel in which antimony chloride had been used. The enamel had been eaten away in very much the same manner that a cutworm works in a garden. It was eaten through in spots around the sides of the vessel slightly above and below the liquid level and looked as if a cutworm had been swimming around on the surface of the liquid, and had been chewing off the enamel on a line about three-quarters of an inch wide all around the surface of the machine. There are cases where enamel chips off due to other causes. In the majority of these cases, however, I think the failures are due to expansion of the base metal and the formation of small cracks in the enamel coating. These cracks are due to pressure expansion or temperature expansion or differentials between the enamel and the base metal, or possibly to the fact that the enamel is not in close contact with the base metal due to a spot of sand or oxide. There are some instances, however, where enameled equipment has failed due to corrosion of the enamel itself.

We can not rely on enamelware especially designed for chemical work not to fail. The manufacture of enamelware which is designed for chemical use is a much more difficult problem than the manufacture of enamelware for dairy purposes, of which many thousand pieces can be made each day. Chemical apparatus is usually large and bulky, and is generally considered to be a special production problem. It is not strange, therefore, that enamelware manufacturers should be more interested in the simpler and more profitable production problems.

Oftentimes during shipment a heavy shock will affect enameled steel, so that there are points at which cracks occur which are absolutely invisible. When subjected to service conditions, however, it is only a short time before the enamel chips off.

Mr. Poste: Mr. Whittaker has just stated that "oftentimes during shipment a heavy shock will affect enameled steel, so that there are points at which cracks occur, which are absolutely invisible. When subjected to service conditions, however, it is only a short time before the enamel chips off."

I feel that the word "shock" hardly applies. If, during transportation or use, mechanical strains are produced in the steel so as to

deflect the metal seriously, the enamel will become fractured. But it would take more than a "shock" to do this. Steel structures to be enameled are designed with at least twice the factor of safety that would be used in the absence of enamel to assure rigidity under normal conditions.

It has also been stated that "chemical apparatus when enameled is . . . generally special. . . ." It is true that a given assembly of equipment may be special, but the elements entering into it are generally quite standard, particularly when cast-iron equipment is involved. Obviously the meeting of needs which the user thinks of as special, but with units which, to the manufacturer, are standard, is a very desirable situation.

MR. ARTHUR L. GARDNER: I would like to ask about this point. I had occasion to use enameled tubes, enameled on the outside, for the purpose of evaporating corrosive liquor, and the enamel failed always along the bottom of the tube. There was no corrosion of the enamel except along the bottom. We attributed it to thermal conditions there, but never obtained a satisfactory solution.

DR. POSTE: Were the tubes to which you refer U-tubes, "hairpins," as we call them?

MR. GARDNER: No; they were straight tubes about 4½ inches in diameter and 6 feet long.

MR. POSTE: It is very difficult successfully to enamel tubing and such work for the chemical trade is undertaken only in very special cases. If there is a seam in the stock due to welding or original imperfections drawn out lengthwise of the tube in its formation, there is liable to be a corresponding defect in the enamel. As a whole the enameling of a tube outside or inside is not desirable. Shorter pieces to be used as fittings can be fairly well processed on the inside. Long lengths are much more troublesome. Possibly these suggestions may have a bearing on the trouble referred to.

MR. R. L. HOLLIDAY: I should like to take exception to the statement made about silver for acetic acid. In Philadelphia there is a silver coil not five years old which has completely failed.

MR. E. L. WILSON: I notice that Mr. Whittaker mentions illium in his paper. We are now using illium in phosphoric acid manufacture and find that in spite of its high initial cost it can be used economically for small parts, such as valve seats, pump impellors, etc.

MR. P. H. GROGGIN: I should like to sustain Mr. Marshall in what

he states regarding the resistance of silver to acetic acid. Silver-lined coils are being used successfully on a large scale in this country in the manufacture of acetanilid and it has been found to be practically the only metal that stands up very successfully. Experience has shown that traces of hydrochloric acid will rapidly destroy equipment designed for glacial acetic acid, and, vice-versa, traces of acetic acid will often destroy equipment designed for the use of hydrochloric acid—witness the destruction of lead coils in an aniline reduction plant when a by-product hydrochloric acid contaminated with acetic acid was used in the reducer.

PRESIDENT HOWARD: I should like to suggest to the other gentleman who has had trouble with silver coils that he should investigate the purity of the silver used. It is quite possible that the silver was not pure.

MR. HOLLIDAY: It was bought for pure silver.

PRESIDENT HOWARD: It would be advisable to investigate it.

MR. MARSHALL: I do know of a case of failure in which the manufacturer of acetic acid had forgotten to make tests for the possible presence of hydrochloric acid, the trouble with the silver being really due to hydrochloric acid coming from the materials used in the original distillation.

PRESIDENT HOWARD: If there is no further discussion we will close this and proceed to the next paper.

The next paper on the program is "The Literature of Chemical Corrosion," by A. E. Marshall.

MR. A. E. MARSHALL (The Literature of Chemical Corrosion): The decision of the Council of the Institute to issue in monograph form the papers read by preceding speakers on various phases of chemical corrosion is considered as contributory evidence to the need for a more extensive literature on corrosion so far as it affects chemical engineering work.

The last decade has witnessed the recognition of chemical engineering as a distinct profession, and a comparison of the curricula of universities and colleges for the years 1912 and 1923 will provide evidence of the present importance placed on the training and industrial value of chemical engineers. Chemical engineering, while it extends into the fields of chemistry and engineering, does not conflict with the work of the chemist or the engineer. It has specific requirements of knowledge which are not essential factors in chemistry or

engineering, one of the most important being a familiarity with chemical corrosion and its effect on materials used in plant construction.

Corrosion resistance from the chemical engineering standpoint is distinct from the requirements for other branches of engineering work, even though the instrumental causes and effects are often similar. A survey of the available literature indicates a decided lack of reliable data, and the growing importance of chemical engineering demands the formulation of some definite plan and sequence of work, which will fill the gaps and permit the compilation of comprehensive and reliable data.

The hand-books of other engineering professions provide information on practically all the problems encountered in the practice of these professions. The mechanical engineer has his Kent, the civil engineer his Trautwine, and the electrical engineer his Foster or Fowle. The chemical engineer does not lack textbooks, but his textbooks are silent on the resistance of plant construction materials to the corrosive action of the raw materials and finished products of the chemical industry. The compilers of the textbooks are not to blame for the deficiency, as they have had no reliable sources to draw from, and the preparation of accurate data on such an extensive subject is too great a task for any one man to undertake.

One of the reasons which has been advanced for the present deficiency in chemical corrosion literature is the disinclination of manufacturers to publish results which might prove useful to competitors. The reading, at this meeting, of a series of papers based on work done in the laboratories of one of the large chemical manufacturing companies is an indication of a broadened spirit in the industry and is in conflict with the expression in Griffith's "Chemical Engineering Design" that "much of the secrecy connected with the prosecution of chemical manufacture relates to matters of chemical engineering alone."

Several of the laboratories attached to educational institutions have contributed excellent material on chemical corrosion and have laid plans for a further extension of this work. The importance of the subject would seem to justify an attempt to interest other institutions which possess the necessary directional and research facilities, in laboratory corrosion determinations, and to formulate some definite plan which would prevent too great an overlapping of effort.

A study of available corrosion data will disclose wide differences

in methods and in the expression of results, so while the figures in one paper will be comparable with each other, they will not be comparable with the results obtained by another worker.

The variants which can enter into laboratory corrosion determinations are so pronounced that comparative results can only be secured by the adoption of a standard method. To illustrate this point, a survey has been made of the methods used by nine investigators who have published corrosion data. No two were in agreement on all points of technique; in fact, there was evidence of widely divergent practice.

Dividing the determinations into stages, variations were found in:

1. Methods of preparing surfaces of material.
2. Methods of suspension in corroding liquid.
3. Degree of submergence.
4. Material at rest or in motion.
5. Corroding liquid at rest or in motion.
6. Constant strength corroding liquid or a fixed initial strength decreasing as the action progressed.
7. Methods of preparing corroded samples before weighing.

The same differences existed in the methods of expressing results, some of the figures used being:

1. Loss expressed as a percentage of original weight.
2. Loss in weight per unit area of exposed surface.
3. Loss in thickness per unit area of exposed surface.

The above summary will indicate the need for standardized methods, not only of performing corrosion tests, but also of expressing the final results.

Corrosion data based on laboratory results are valuable, but there is also a very definite need for performance records based on actual plant experiences over reasonably long periods of time. The provision of a useful literature of chemical corrosion, therefore, depends on research laboratory records and plant performance reports under usual and unusual manufacturing conditions.

So far, the needs of the chemical engineer for reliable corrosion data have been stressed, and a suggestion made as to the desirability of interesting research graduates in corrosion work. It has also been shown that wide differences in methods and expressions of results exist, and that there is a need for plant performance data.

There are several agencies already active in the collection of gen-

eral corrosion data, including the National Research Council, the American Society of Testing Materials, and the Prime Movers Association.

None of these bodies are undertaking the compilation of data designed primarily for the use of chemical engineers, and there is, of course, no reason why they should do so. It is recognized, on the other hand, that records of general corrosion work, as, for instance, corrosion through mine waters, hydrolized chlorides in boiler waters, etc., will have a bearing on certain phases of chemical corrosion, and that results of many strictly chemical problems will be of value to workers in the general field. Thus there is every reason why efforts made toward the establishment of authentic chemical corrosion records should be carried on with full recognition of the value of coöperation with other agencies now investigating general corrosion problems, without it acting as a deterrent to the establishment of a "clearing house" for chemical corrosion data.

The Constitution of the Institute of Chemical Engineers contains a clause which states that one of the objects of the organization shall be: "To publish and distribute such papers as shall add to classified knowledge in chemical engineering and shall increase industrial activity."

In the author's opinion the Institute could undertake no more valuable work than has been outlined in this paper, and suggests a committee be formed, to be known as the Chemical Corrosion Committee, and that this committee be charged with the duties of:

Coördinating and standardizing methods for chemical corrosion tests.

Collecting and checking available data based on laboratory tests and plant performances.

Developing a systematic scheme of research on the corrosion of chemical plant materials.

Interesting research workers in corrosion problems, and when desired assigning research studies.

It is his further thought that through the work of this committee the Institute would sponsor the publication of a series of monographs on "Chemical Corrosion."

MR. WHITTAKER: I think the Chairman of our Corrosion Committee of the National Research Council, Mr. Corse, is here, and he may have something to say regarding the correlation of information.

A MEMBER: Mr. Corse has just stepped out. Dr. Lathrop is here, of the American Society for Testing of Materials.

DR. ELBERT C. LATHROP: I want to take this opportunity to bring to your attention the work done by the committee of the American Society of Testing Materials, known as B–3. This work was undertaken last year and the first step was to draw up a very elaborate questionnaire which was sent out to some 250 men, and companies, known to be interested in the question of corrosion, both from the standpoint of atmospheric and chemical corrosion. Only a relatively small number of complete replies were received, but these will probably be drawn up in the form of monograph at a later date to be presented in the transactions of that Society.

Committee B–3 is very anxious to obtain the coöperation of the chemical engineers, because the chemical engineers will eventually say what non-ferrous metal will be used in the construction of apparatus. The aim of the committee is not to undertake research work on corrosion, but to try and work out satisfactory definitions for the terms used and to try to draw specifications for testing of a few of the best known kinds of corrosion. These tests will then probably be submitted to the various companies and individuals, and an effort made to determine how well various workers in the different laboratories can duplicate results on the same metal under standardized conditions.

PRESIDENT HOWARD: What is your idea, Dr. Lathrop, regarding the appointment of such a committee as Mr. Marshall has suggested?

DR. LATHROP: I think Mr. Corse is in a better position to answer that, because he is correlating the work on corrosion with other engineering societies. I know that this work is being carried on under a variety of topics, and in considering what Committee B–3 would take up we went over with Mr. Corse what other societies are doing, and we are confining our efforts to a single phase of the question. If Mr. Corse comes in I think it will be well to have him talk to us.

MR. MARSHALL: Prior to the arrival of Mr. Corse I should like to lay emphasis on one fact, and that is that the American Institute of Chemical Engineers should at some time or other decide to do something for itself, and not work solely through other institutions. It is quite true that the National Research Council can collect much valuable material on corrosion, but I do not think the facilities of the National Research Council can compare with the facilities of this

Institute in the matter of collecting definite information on corrosion, particularly the plant phases of it as obtained in actual works' practice. I should like to see a monograph on chemical corrosion go out from this Institute, carrying the Institute's endorsement, as a first effort toward meeting the needs of our own profession.

PRESIDENT HOWARD: Mr. Marshall, there is no motion before the meeting. Perhaps you will put your recommendation in the form of a motion, and then it can be discussed.

MR. MARSHALL: I would move that a committee be formed, to be known as the Chemical Corrosion Committee, and that this committee be charged with the duties of:

Coördinating and standardizing methods for chemical corrosion tests.

Collecting and checking available data based on laboratory tests and plant performances.

Developing a systematic scheme of research on the corrosion of chemical plant materials.

Interesting research workers in corrosion problems, and when desired assiging research studies.

PRESIDENT HOWARD: We should like to hear from Mr. Corse, and get his opinion as to whether there will be any duplicating of effort between such a committee and the National Research Council.

MR. WILLIAM M. CORSE: Mr. President, I just came in and did not hear the entire remarks of Mr. Marshall, but I am quite sure that any work which we contemplate at the National Research Council will not in any way interfere with the scheme which Mr. Marshall has outlined. The sole purpose of the Corrosion Committee of the National Research Council is to do what is being done here this morning, to stimulate interest in the subject and get committees to work on it. In other words, our Committee on Corrosion at the Council is a steering committee only, and has no intention of taking work away from technical societies such as this. If we can interest technical societies in this subject, to do what Mr. Marshall's motion suggests, it would be exactly what we would like to see done. I understood that the suggestion was made that a committee from this Institute consider the determination of a practical test for corrosion. I am not sure whether that matter was touched on by Dr. Lathrop, but I might say that our committee of the Council asked the American Society for Testing Materials to organize a committee on corrosion

of non-ferrous metals and alloys, about a year ago. They already had a Committee on Corrosion of Iron and Steel, known as A–5. The new committee which we suggested they organize is known as B–3, and Dr. Lathrop of this Institute is chairman of the committee.

The particular thing which we asked that committee to do was to determine a standard test for corrosion. If the members of the corrosion committee of this Institute are willing to help in this work, I am sure Dr. Lathrop's committee would be glad to coöperate. I suggest that the committee from this Institute coöperate fully with the committee from the American Society for Testing Materials.

To repeat what I said before, the National Research Council committee aims to interest people in this subject and to bring about the appointment of committees just as has been suggested by Mr. Marshall, so if we can act as a coördinating body, avoiding duplication, we have done what we planned to do. I hope that answers your question, Mr. President.

Dr. Jerome Alexander: In rising to support Mr. Marshall's motion, I want to point out that the problem which this touches is a highly specialized one, dealing with chemical corrosion. Professor Jackson has just told me that there is a committee from the United Engineering Societies dealing with corrosion in general, but that the committee is dealing with corrosion by the elements, ordinary meteorological elements, while the committee Mr. Marshall proposes is to study high specialized work. I take it for granted that any committee appointed under Mr. Marshall's motion would naturally get in with any other committees.

Dr. Reese: I am very much in favor of Mr. Marshall's motion and see no reason why we might not coöperate. I should think it very desirable to put the chairman of the committee from this association on the committee of the National Research Council if that is possible.

Mr. Corse: I think it is possible.

Dr. Reese: It would be desirable to have a member on each of these committees, who would either be members or would be directed to attend the meetings of the Council, and other organizations in this matter.

Mr. Corse: If the Secretary will send me a letter suggesting that the chairman of this proposed committee be added to the Research Council committee, I shall be glad to take the necessary steps to have that done.

Dr. Lathrop: The Committee on Testing Materials is largely made up of members of this Institute.

(Thereupon the question was put, and the motion presented by Mr. Marshall was adopted without dissent.)

Mr. Paul D. Merica (communicated): I am very glad that the Institute is devoting some of its time to consideration of this problem of corrosion, as evidence of the increasing realization by its members of its significance in connection with chemical manufacturing. As Messrs. Calcott and Whetzel remark, the success or failure of a process may often depend on the proper selection of the equipment materials.

Once this fundamental fact is realized the importance of developing precision methods of measuring corrosion resistance becomes at once apparent, and our appreciation is due the authors for the constructive work they have done in making critical studies of such methods and finally applying them to a variety of chemicals and materials commonly in use.

I fully believe that the authors have demonstrated that if properly executed, with control of known factors, a corrosion test, at least of the complete immersion type, may yield precise results possible of duplication at any time. There may still, however, be some disposition to doubt whether much of practical value may be inferred from such tests in view of the experience which most of us have had in predicting service behavior from laboratory tests. I think we should remember, however, that the art of mechanical testing of materials once went through almost the same course which corrosion-resistance testing is now taking. At one time, and not more than forty years ago, tensile tests made in one laboratory would not check those made in others, and it was not until the practice of such testing had been standardized, partly by private experiment and partly through the instrumentality of technical societies such as the Society for Testing Materials, that agreement was reached.

Furthermore, no one would deny today the value of the usual mechanical tests of materials, yet our course of inference from their results to the service behavior of the materials is still not entirely clear and depends on practical experience. And thus will it be with corrosion-resistance testing; our first task ended—that of the development of precise and duplicable methods of testing—the next and greater one will be to learn how to apply the results in practice. I

am thoroughly convinced that within a few years our effective knowledge of corrosion will be revolutionized, and certainly the authors have done much to show us the way.

Dr. Lathrop has described the purpose and work of a new committee of The American Society for Testing Materials: B–3 on the Corrosion of Non-ferrous Metals. It was my fortune to be chairman of a subcommittee of that committee, charged with making a survey of the practice and ideas of those in this country doing corrosion work on such materials. It was very encouraging to note the active interest in the subject and to realize how rapidly progress is being made by individuals in all industries in the practice of corrosion testing.

Dr. G. W. Thompson (communicated): I have been reading over very carefully the papers entitled "Materials of Construction for Chemical Apparatus," by Harold F. Whittaker, and "Laboratory Corrosion Tests," by W. S. Calcott and J. C. Whetzel. I believe that they contain some of the very best material which has been contributed to assist the work of the chemical engineer. I have concluded that it would be unwise for me to discuss either of these papers in detail. They represent an amount of work and research that is monumental in character. There are two thoughts, however, that present themselves to my mind:

1. As many of the materials used in chemical manufacturing apparatus differ in purity or composition, it would be exceedingly desirable if work could be done, preferably in a coöperative way, to determine the effect of these impurities upon the suitability of the materials for the particular uses they are to be put to. For instance, the presence of a small amount of copper in sheet lead used for acid chambers is generally considered desirable. There are differences of opinion upon this subject, both as to the desirability of copper and as to the quantity of copper that gives the best results. More information on this subject is desired.

2. Might it not be desirable for the Institute to have a standing committee on materials to be used in chemical manufacturing apparatus, which committee would be a kind of clearing house for data and also help in the development of coöperative work?

Mr. Percy C. Kingsbury (communicated): This paper is a very useful addition to the literature of corrosion. A great deal of what has already been published on this subject consists of data compiled

from laboratory work that does not parallel the conditions met with in the plant and which therefore is of little value to the plant operative.

The advantage of this paper is that we are told definitely what materials can be used to meet any specific corrosion problem and are not left to draw our own conclusions from the mass of curves and tables.

The author has, as he states, attempted to cover a very wide range, and in doing so has not considered such important factors in the selection of the material for chemical apparatus as comparative price and the practicability of working up the material into the shapes and sizes desired.

Furthermore, the various materials are mentioned without reference to their relative importance. In most problems relating to the manufacture or handling of corrosive materials to which the common metals are not applicable the first thought of the plant superintendent is chemicalware and the ferro-silicon alloys. Most of the acids referred to by the author are, as a rule, manufactured on the industrial scale in chemicalware apparatus, which is, however, mentioned only casually in this paper. Perhaps the author assumes that the use for chemicalware for such purposes is self-evident. Some of the materials referred to under " special metals and equipment " which are not much more than interesting curiosities of very limited application in the plant are given more prominence than the materials commonly employed in industrial work.

This is not intended to be a criticism of the paper, as there is naturally more to be said about a comparatively new material than about those with which everybody is familiar. However, it will undoubtedly be used for reference where corrosion problems are to be solved, and it is hoped that these remarks will prevent the young chemical engineer from spending his appropriation on materials that are more or less of an experimental nature instead of using products that have for many years given satisfactory service under similar conditions to those he has to meet.

# AUTOMATIC FRACTIONATING COLUMNS

By Wm. A. Peters, Jr.

Read at Wilmington, Del., Meeting, June 22, 1923

The first fractional distillations were carried out in batch stills, and the operation required careful watching at all times and repeated distillations to obtain a high degree of separation. Later, the continuous rectifier was developed for certain fractionations and,

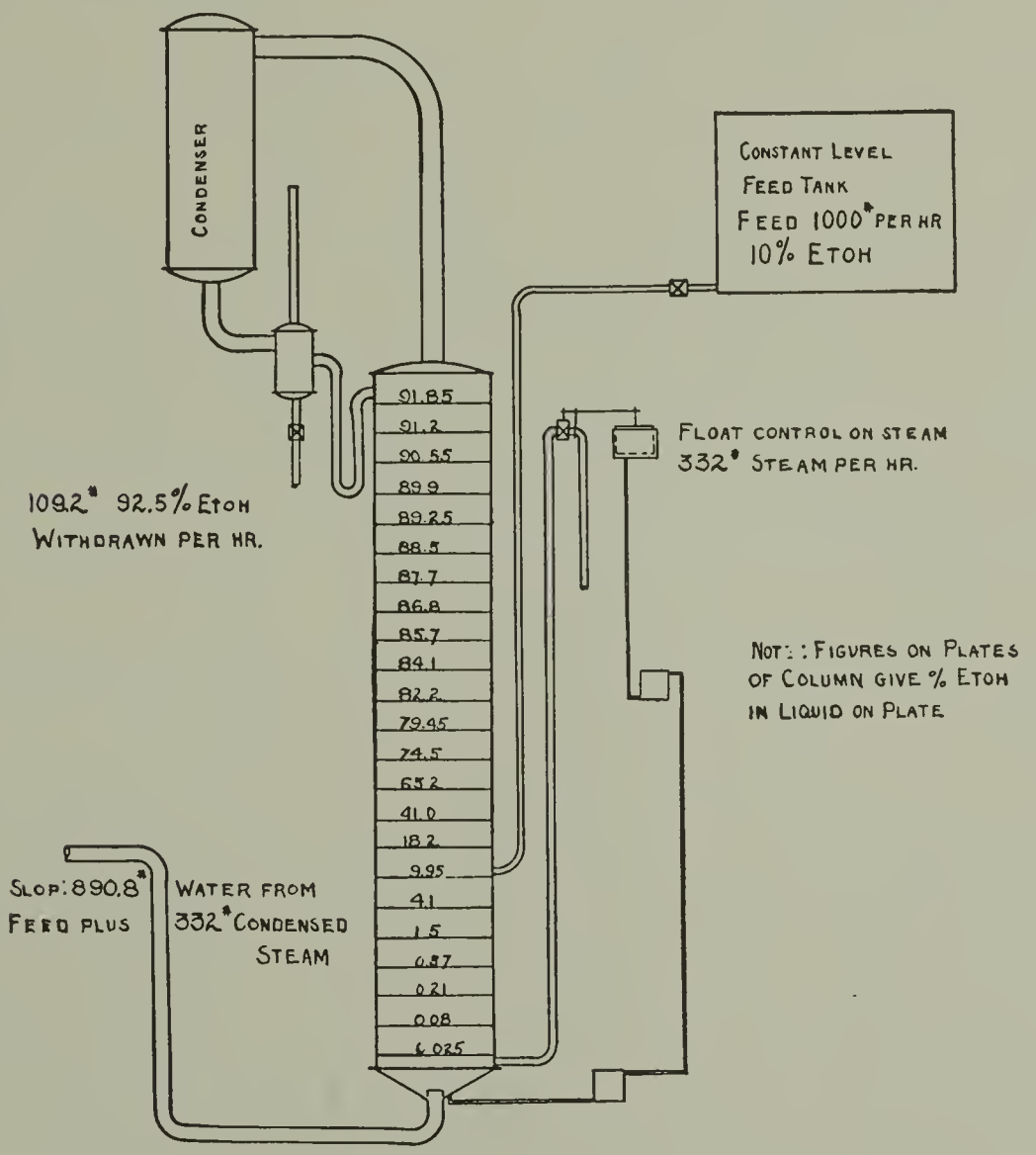


FIG. 1. Standard Continuous Rectifier

since the rectifier might be regarded as a series of small stills operating simultaneously, the labor required for a given output was considerably reduced.

If the composition of the feed and all other conditions were maintained absolutely constant, it might be possible to run a con-

tinuous rectifier indefinitely without any attention and obtain a satisfactory product. The important details of such a rectifier for separating alcohol and water are shown in Fig. 1. The divisions shown in the column represent theoretical plates.[1] A theoretical plate is defined as one on which the liquid covering it is of the same composition throughout, while all the vapor rising from it is in equilibrium with this liquid. It therefore represents a certain height of column rather than one or more actual plates of a plate column, and this same conception can be applied equally well to a packed column. In fact, all our small automatic columns are packed with

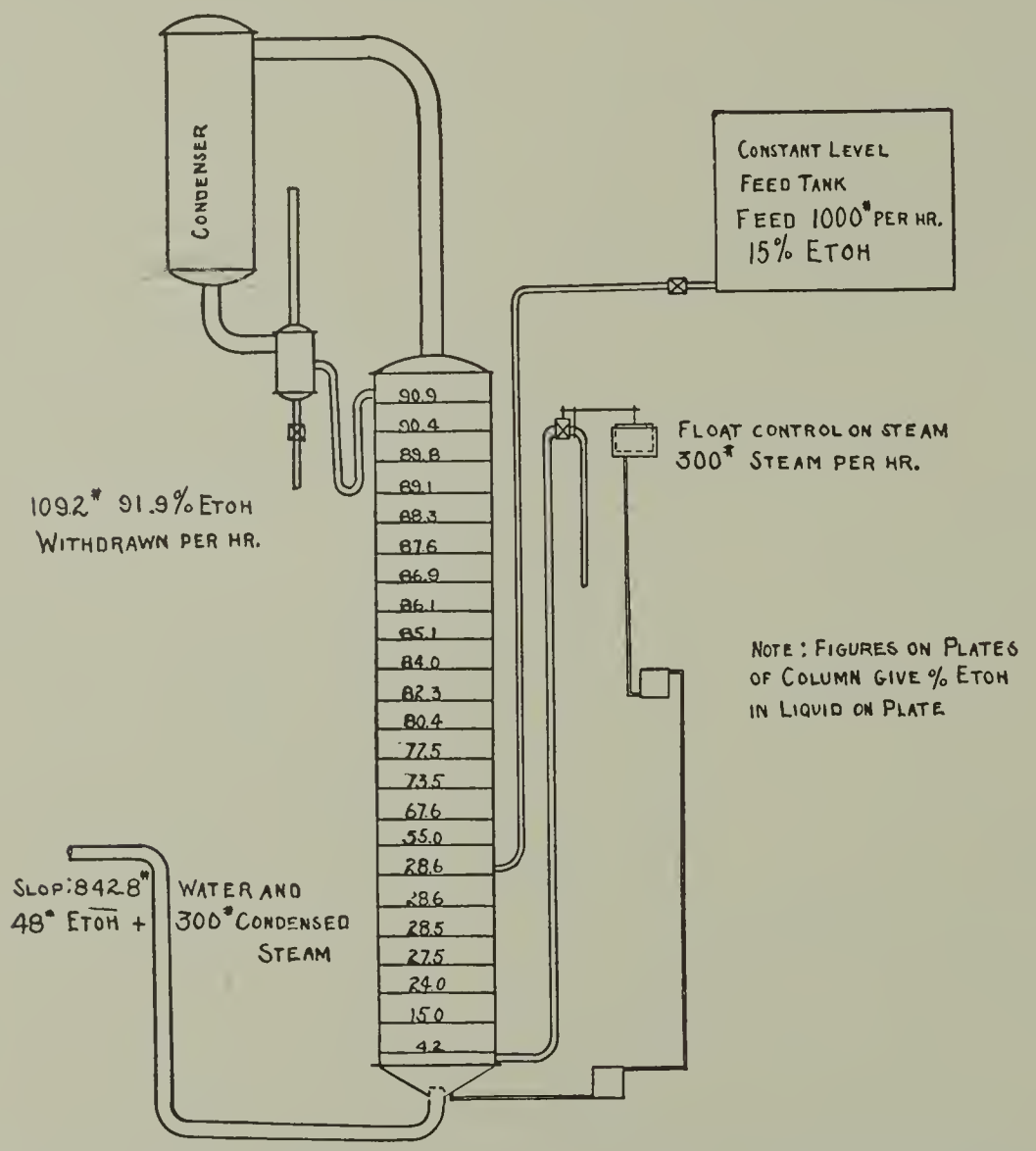


FIG. 2. Standard Continuous Rectifier with Excess Alcohol in Feed

glass rings, a type of construction that is much cheaper than the plate column for the smaller units. It will be noted that the steam supply is controlled by a float operating from the pressure at the base of the column so that this pressure is maintained constant.

[1] *J. Ind. Eng. Chem.* **15**, 476–9 (1923).

It would be easy to maintain both the feed and the draw-off constant, but the composition of the feed might vary. If, with constant feed, the amount of alcohol in the feed is increased, the liquid and vapor on the plates of the column will become richer in alcohol, and since a richer liquid in the column gives more back pressure for a given steam supply to the base, the steam will be cut down and the rectifier will operate as shown in Fig. 2 until the feed is checked. Not only will the distillate be poorer alcohol, but all the excess alcohol in the feed will be lost in the slop.

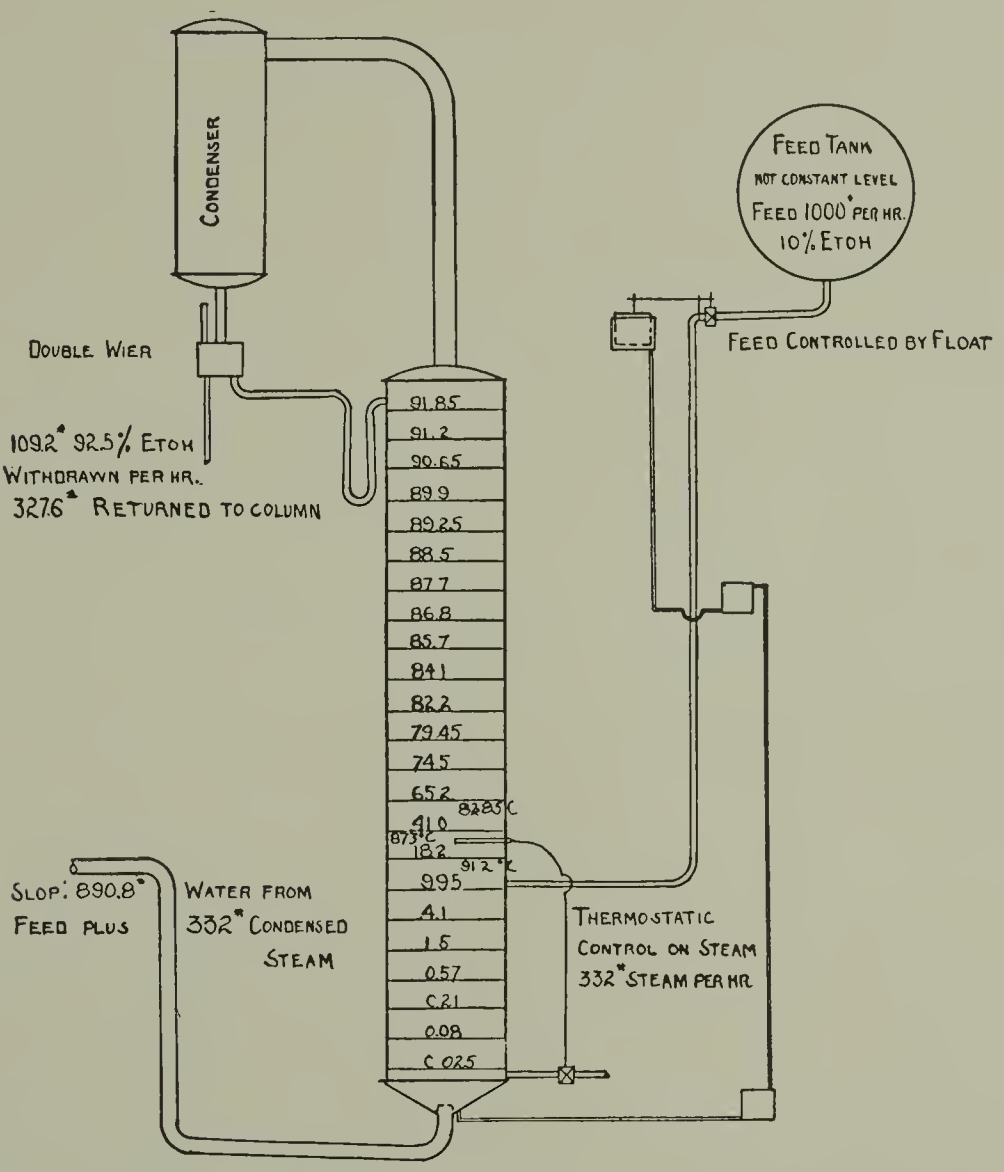


FIG. 3. Automatic Rectifier

The operation of the column can be made fully automatic in several ways, so that such changes in feed composition will be taken care of. One method is shown in Fig. 3. Here a double wier is placed in the distillate line so that the ratio of distillate withdrawn to distillate returned to the column as reflux remains constant (0.408 to 1 in this case), and a thermostatic control is put on the

steam supply to maintain a given temperature at some point in the column. The feed is controlled by a float operated from the base of the column. This method of control insures that as long as sufficient feed is available it will be supplied at the maximum allowable rate. Of course, if less is available it will simply run to the column as supplied.

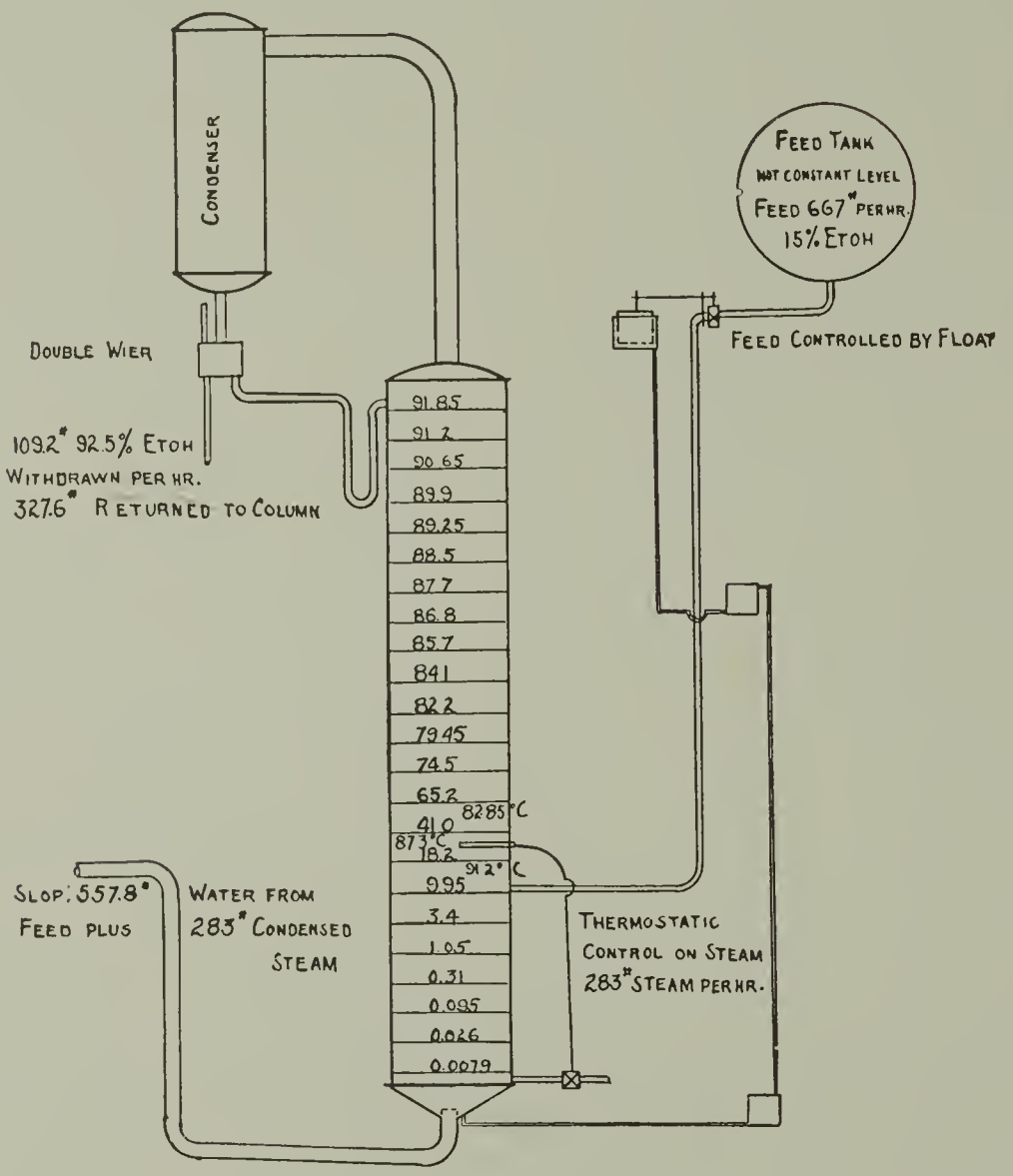


FIG. 4. Automatic Rectifier

After the column has come to equilibrium under the conditions given in Fig. 3 (same feed and steam supply as shown in Fig. 1), let the amount of alcohol in the feed be increased to 15 per cent. The first effect will be an enrichment of alcohol on the plates near the feed plate. This will cause the temperature at the thermostat to drop and more steam will be admitted to the column. But it will also cause the pressure at the base of the column to rise, which will raise the float regulator and reduce the feed. Although the feed is richer, the column will not handle a greater amount of alcohol for

the same back pressure at the base, since it should already be working very nearly to capacity at the top plates where the liquid and vapor are rich in alcohol. A very slight increase in steam will therefore start the column to load near the top and run the pressure up at the base. Hence, when a balance is finally reached, the conditions in the upper part of the column will be almost exactly the same as before the feed was changed. The conditions in the lower part of the column will be shown as in Fig. 4.

If the alcohol in the feed is reduced to 5 per cent, the column will no longer deliver 109.2 lbs. of distillate, since a much larger amount of steam is required to heat the feed. This will cause an increase of back pressure in the lower section of the column. When equilibrium is finally reached, we may be getting about 100 lbs. of distillate from 1850 lbs. of feed. The slop will run 0.21 per cent alcohol. In case it is necessary to take care of such wide variations of feed, a small addition can be made to the bottom of the column. The equivalent of five extra theoretical plates below the feed plate will bring the slop down to 0.01 per cent in this case.

It is seen that by maintaining the ratio of reflux to distillate constant, the composition of the distillate will be absolutely independent of the composition of the feed. The automatic rectifier will work just as well on many other mixtures, such as alcohol and acetone, acetone and water, ammonia and water, and it will work nearly as well on any mixture of two liquids. It has also been arranged to make separations of mixtures containing more than two components.

Variations of this arrangement have been used. For example, where it was required to keep a given amount of distillate on hand, the feed was controlled by the level of distillate in a storage reservoir. One of these units has operated for over two months without any attention whatever.

Patent applications covering this rectifier have been made.

EXPERIMENTAL STATION,
E. I. DUPONT DE NEMOURS & CO.,
WILMINGTON, DEL.

# SOME FACTORS INFLUENCING THE DESIGN OF ABSORPTION APPARATUS

By R. T. HASLAM, W. P. RYAN, H. C. WEBER

Read at the Richmond Meeting, Dec. 7, 1923

In the design of an absorption system we are usually concerned with the size of tower or scrubber necessary to absorb a given amount of material per hour under fixed terminal conditions; e.g. concentration of entering gas, temperature of scrubbing liquid, per cent recovery, etc.

Oftentimes, in addition, knowledge is desired of how a change in one or more of these terminal conditions will affect either the size of unit required, the capacity of a given unit or the per cent of material lost in the exit gases. Both problems involve the rate at which matter is transferred from a gas to a liquid or vice versa. In this, as in the case of the flow of electricity, and the flow of heat, the rate of transfer is proportional to a "driving force." In the flow of heat this driving force is the temperature difference between the hot and the cold body; in electricity, the driving force is the potential difference or E.M.F. existing between the two points; in absorption it is the distance the gas-liquid system is from equilibrium. In the case of the flow of electricity the resistance also influences the quantity of electricity that will flow in a given time. With the transfer of heat the same situation holds true, the amount of heat that flows from a hot body to a cold one in a unit time is not only proportional to the temperature difference (driving force), but it is also inversely proportional to the resistance through which the heat must flow. So too with the transfer of material in absorption apparatus the rate of flow of the material from one phase to the other is not only proportional to the driving force (distance the system is from equilibrium) but it is also inversely proportional to the resistances between the gas and liquid, which are, as shown by Whitman and Keats,[1] the gas film and the liquid film. These film resistances are not due to actual stationary films through which heat flows by conduction and material by diffusion, but in either case at present we view these resistances as equivalent to stationary films of varying thickness.

The similarity between the flow of heat and the transfer of material from a gas to a liquid phase or vice versa does not end with the fact that each is proportional to a driving force and inversely proportional to a resistance. It has been shown, also, that the major resistances in both cases are equivalent to gas and liquid film resistances, and, in addition, W. K. Lewis [2] has shown that under certain limiting conditions the coefficient of material transfer is proportional to the coefficient of heat transfer. In view of this similarity it seems advisable to study the rate of absorption (or transfer of material from gas to liquid) in a manner similar to the study of the older science, the flow of heat.

Newton's Law on the flow of heat is as follows:

$$\frac{dQ}{d\theta} = \left(\frac{hA}{dl}\right) dt \qquad (1)$$

where $dQ/d\theta$ is the quantity of heat flowing per unit of time through the area $A$ of thickness, $dl$, when the driving force or temperature difference is $dt$. The constant $h$ is the coefficient of heat conductivity. This equation has the same form as Ohm's Law where:

$$\text{Quantity (current)} = \frac{\text{Driving force (E.M.F.)}}{\text{Resistance}}$$

where $dQ/d\theta$ is the quantity factor, $dt$, the driving force and $dl/hA$ is the resistance. In the transfer of heat $1/h$ is the *total* or *overall* coefficient of resistance, often composed of three resistances, the intervening wall and the fluid film resistances on either side of the wall. An exact knowledge of the laws governing the flow of heat was brought about, not by investigating the overall coefficient of resistance, $1/h$, but by determining the coefficients of resistance of the walls and the films separately and noting how such variables as materials, velocity, temperature, etc., changed each resistance. Knowing each of the resistances one may easily calculate the overall resistance. In heat transfer, the main problem is the determination of the two film coefficients. As shown by Weber [3] the coefficient of heat transfer for *gaseous films* (forced convection) is as follows:

$$h_g = \frac{0.88(V_m)^{0.8}(T)^{0.5}(S)^{0.2}(C_p)}{M^{0.3}} \qquad (2)$$

where $h_g$ = coefficient of heat transfer through the gaseous film
$V_m$ = the mass velocity of the gas
$T$ = gas temperature in degrees Centigrade absolute

$S$ = surface factor $\left(\frac{\text{area}}{\text{volume}}\right)$

$C_p$ = specific heat of gas at constant pressure
$M$ = molecular weight of gas

McAdams and Frost [4] have shown that the coefficient of heat transfer through a *liquid film* is as follows:

$$h_L = \frac{23.3K(DVZ)^{0.8}}{D} \tag{3}$$

where $h_L$ = coefficient of heat conduction
$K$ = Thermal conductivity of stationary liquid
$D$ = Diameter of pipe through which liquid flows
$Z$ = Fluidity of film on pipe relative to water
$V$ = Average mass velocity of liquid

From these two equations it is seen that the resistance of the gaseous film ($1/h_g$) is inversely proportional to the gas velocity to the 0.8 power, and that the resistance of the liquid film ($1/h_L$) is inversely proportional to the 0.8 power of the liquid velocity and the 0.8 power of the fluidity.

Turning now to material transfer or absorption, the rate of absorption of one material from a stream by another stream of material flowing counter-current to the former may be expressed in a manner similar to the flow of heat (Equation (1)).

$$\frac{dW}{d\theta} = kaV\Delta P \tag{4}$$

where $\frac{dW}{d\theta}$ = weight in lbs. of material being absorbed per minute

$\Delta P$ = the driving force or distance from equilibrium, often expressed as pressure difference between the partial pressure of solute in gaseous and liquid phases expressed in mm. of Hg.

$V$ = Total interior volume of apparatus in cu. ft.

$ka$ = The overall absorption coefficient equivalent to the lbs. of gas absorbed per minute per cu. ft. of volume per mm. Hg partial pressure difference when $\Delta P$ and $V$ are expressed as above.

This differential may be expressed as an average equation of rate

$$\frac{W}{\theta} = ka\,V(\Delta P)_{\text{ave.}} \qquad (4a)$$

When the gas obeys Henry's law and the temperature effects are small, the $\Delta P_{\text{ave.}}$ is the log mean of the pressure differences between the partial pressure of the solute in the gaseous and liquid phases taken at the ends of the system.

In this equation the overall coefficient of absorption, $k$, is coupled with the unknown area through which absorption takes place, $a$. The overall coefficient, $ka$, is proportional to $1/(R_g + R_L)$ where $R_g$ is the resistance of the gas film and $R_L$ is the resistance of the liquid film.

The following experimental work, absorbing $SO_2$ from burner gas by water, was carried out with the view of studying the effect of gas velocity and temperature on the rate of absorption, hoping thereby to obtain more information regarding the nature of the film resistance and to see if the resultant overall coefficient of absorption, $ka$, could be explained on the basis of two films, gaseous and liquid, in series, each obeying a law similar to that governing the flow of heat through similar films.

## Experimental Results

*Series I* was made with an unpacked tower 8 in. diam. by 30 in. high, through which water was fed down the inside wall at a rate equivalent to 16.8 lbs. per sq. ft. of cross sectional area per minute at a constant temperature of approximately 58°F. The velocity of the gas was varied from 0.084 ft. per second to 0.396 ft. per second and the rate of absorption, absorption coefficient and percent absorption is given in Table I. The absorption coefficient, $ka$, is plotted versus gas velocity in Fig. 1.

*Series II* was made in the same tower as Series I but the water was sprayed in at the rate of 32.6 lbs. per sq. ft. of cross section per minute. The temperatures were approximately constant at 55° F.

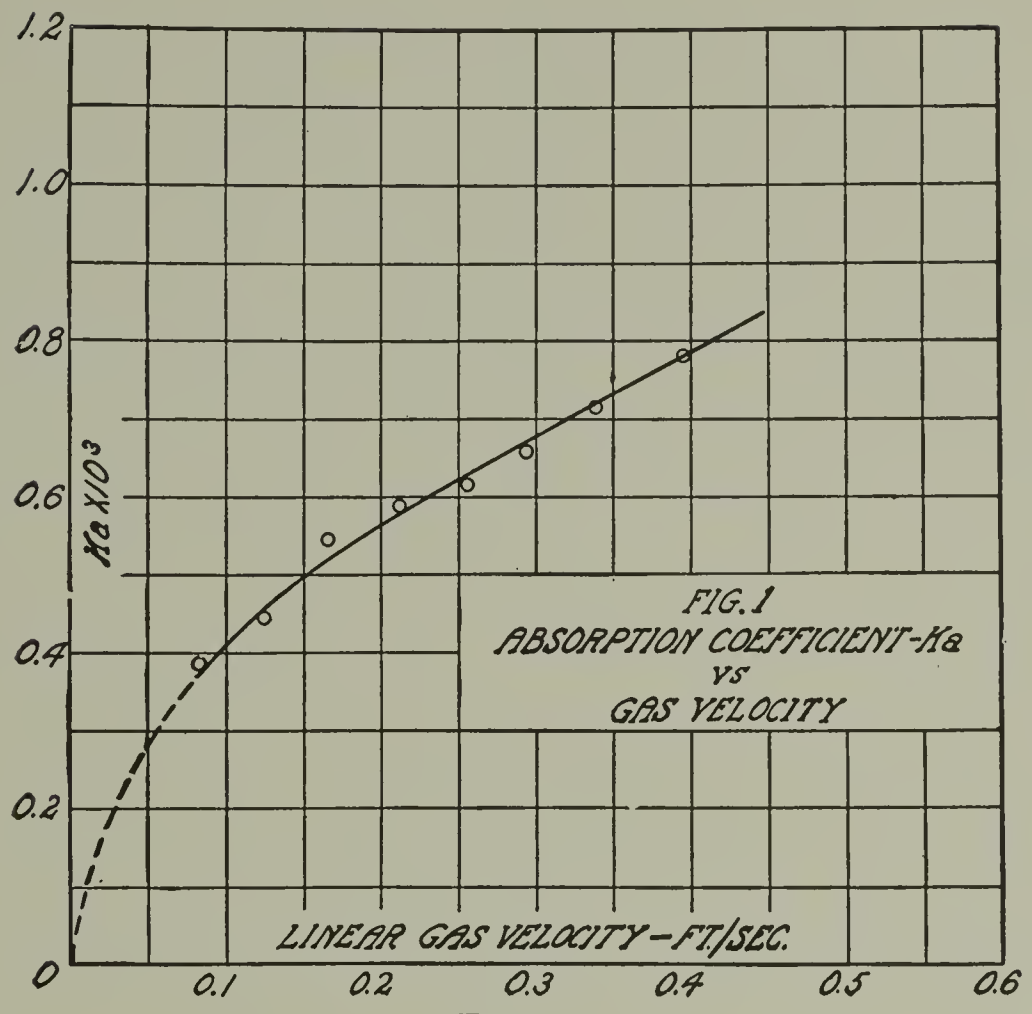
1.2
1.0
0.8
0.6
0.4
0.2
0
Ka X/0³
FIG. 1
ABSORPTION COEFFICIENT-Ka
VS
GAS VELOCITY
LINEAR GAS VELOCITY-FT./SEC.
0.1
0.2
0.3
0.4
0.5
0.6

FIG. 1.

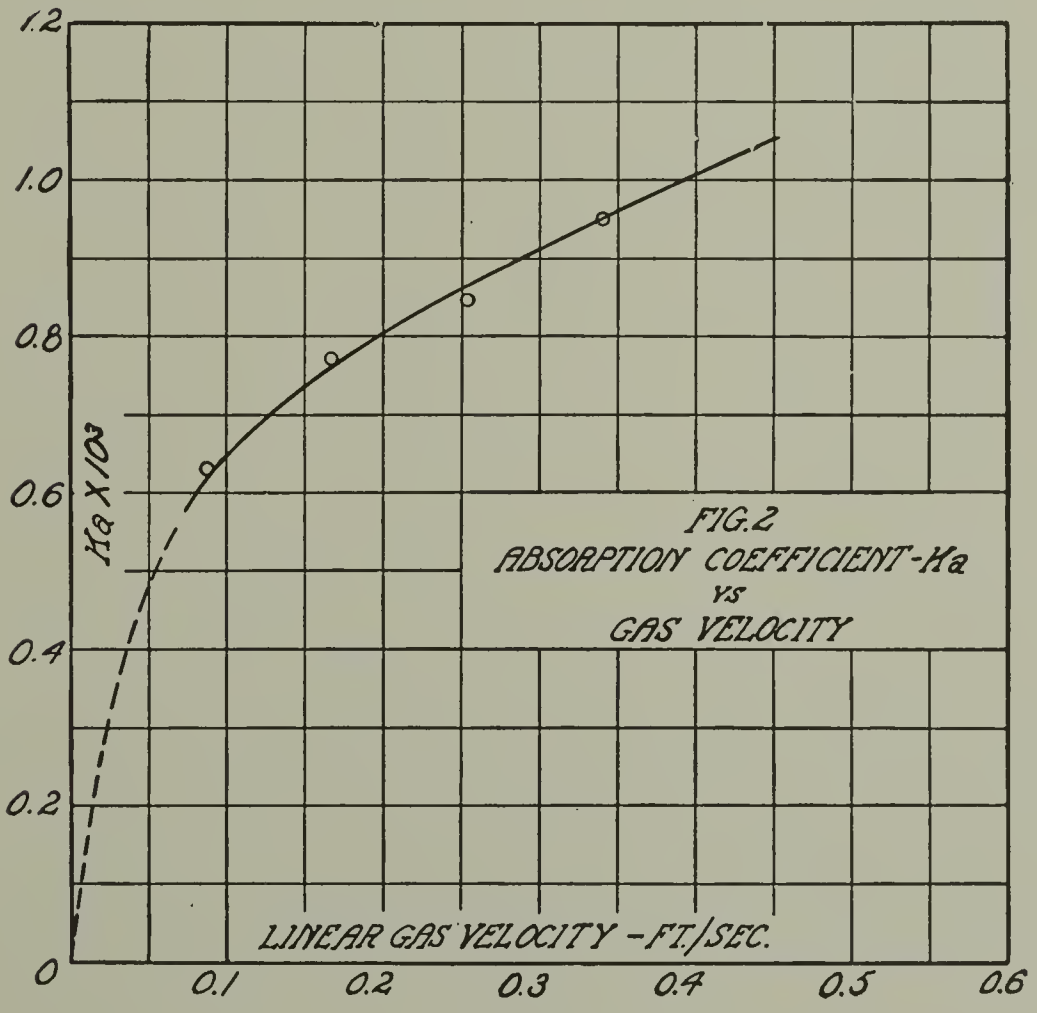
1.2
1.0
0.8
0.6
0.4
0.2
0
Ka X/0³
FIG.2
ABSORPTION COEFFICIENT-Ka
VS
GAS VELOCITY
LINEAR GAS VELOCITY-FT./SEC.
0.1
0.2
0.3
0.4
0.5
0.6

FIG. 2.

TABLE I

RATE OF ABSORPTION *vs.* GAS VELOCITY

*Series I*

| Gas Velocity ft./sec. | $ka \times 10^3$ | Lbs. $SO_2$ Absorbed/min. $\frac{dW}{d\theta}$ | $\Delta P$ mm. Hg | Per Cent of Total $SO_2$ Absorbed |
|---|---|---|---|---|
| 0.084 | 0.39 | 0.0134 | 39.2 | 47.3 |
| 0.125 | 0.44 | 0.0162 | 42.0 | 40.5 |
| 0.166 | 0.55 | 0.0204 | 42.5 | 30.0 |
| 0.213 | 0.59 | 0.0208 | 40.5 | 31.6 |
| 0.256 | 0.61 | 0.0221 | 41.5 | 30.0 |
| 0.294 | 0.66 | 0.0252 | 43.7 | 26.0 |
| 0.339 | 0.71 | 0.0270 | 43.5 | 24.5 |
| 0.396 | 0.78 | 0.0286 | 42.0 | 17.0 |

The gas velocity was varied from 0.088 ft. per second to 0.341 ft. per sec. The resultant data similar to that taken in Series I are shown in Table II and in Fig. 2 *ka* is plotted against gas velocity.

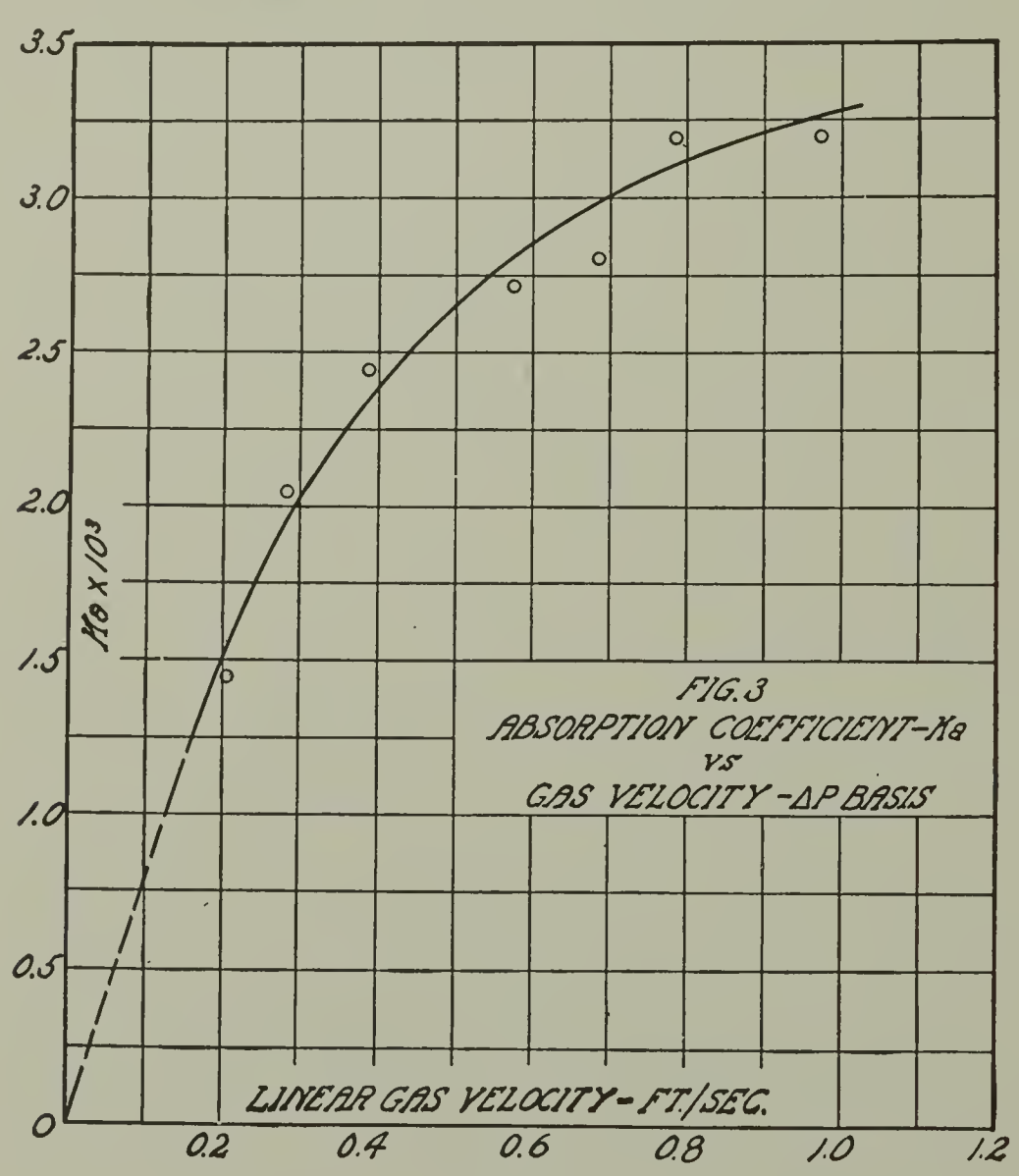


FIG. 3.

TABLE II

*Series II*

| Gas Velocity ft./sec. | $ka \times 10^3$ | Lbs. $SO_2$ Absorbed/min. $\frac{dW}{d\theta}$ | $\Delta P$ mm. Hg | Per Cent of Total $SO_2$ Absorbed |
|---|---|---|---|---|
| 0.088 | 0.63 | 0.0225 | 41.1 | 68 |
| 0.167 | 0.77 | 0.0304 | 45.2 | 49 |
| 0.254 | 0.85 | 0.0382 | 51.5 | 34 |
| 0.341 | 0.95 | 0.0438 | 52.8 | 30 |

*Series* III was made with the same tower packed with 1 in. diam. coke, the water rate being 32.3 lbs. per sq. ft. of cross section per minute and the temperature approximately 56°F. The gas velocity was varied from 0.204 to 0.976 ft. per sec. and the results are shown in Table III, and in Fig. 3 the absorption coefficient, *ka*, is plotted against gas velocity.

TABLE III

Effect of Linear Gas Velocity on Absorption

| Gas Velocity ft./sec. | $ka \times 10^3$ | Lbs. $SO_2$ Absorbed/min. $\frac{dW}{d\theta}$ | $\Delta P$ mm. Hg | Per Cent $SO_2$ Absorbed | Per Cent Equilibrium Reached |
|---|---|---|---|---|---|
| 0.204 | 1.46 | 0.0278 | 21.8 | 40.1 | 16.2 |
| 0.282 | 2.06 | 0.0398 | 22.2 | 41.2 | 24.3 |
| 0.389 | 2.45 | 0.0516 | 24.0 | 39.1 | 30.0 |
| 0.484 | 2.71 | 0.0614 | 26.2 | 39.2 | 37.2 |
| 0.578 | 2.72 | 0.0686 | 29.1 | 34.1 | 39.0 |
| 0.684 | 2.79 | 0.0770 | 31.4 | 32.4 | 43.8 |
| 0.785 | 3.17 | 0.0833 | 30.1 | 31.6 | 48.3 |
| 0.976 | 3.18 | 0.0933 | 33.2 | 26.7 | 52.8 |

*Series IV* was made with a tower 8 in. diam., 30 in. high, packed with 3 in. x 3 in. spiral tile, the water rate being 32.1 and the temperature approximately 60°F. The gas velocity was varied from 0.1 ft. per sec. to 0.565 ft. per sec. The results are given in Table IV and in Fig. 4 the absorption coefficient, *ka*, is plotted against gas velocity.

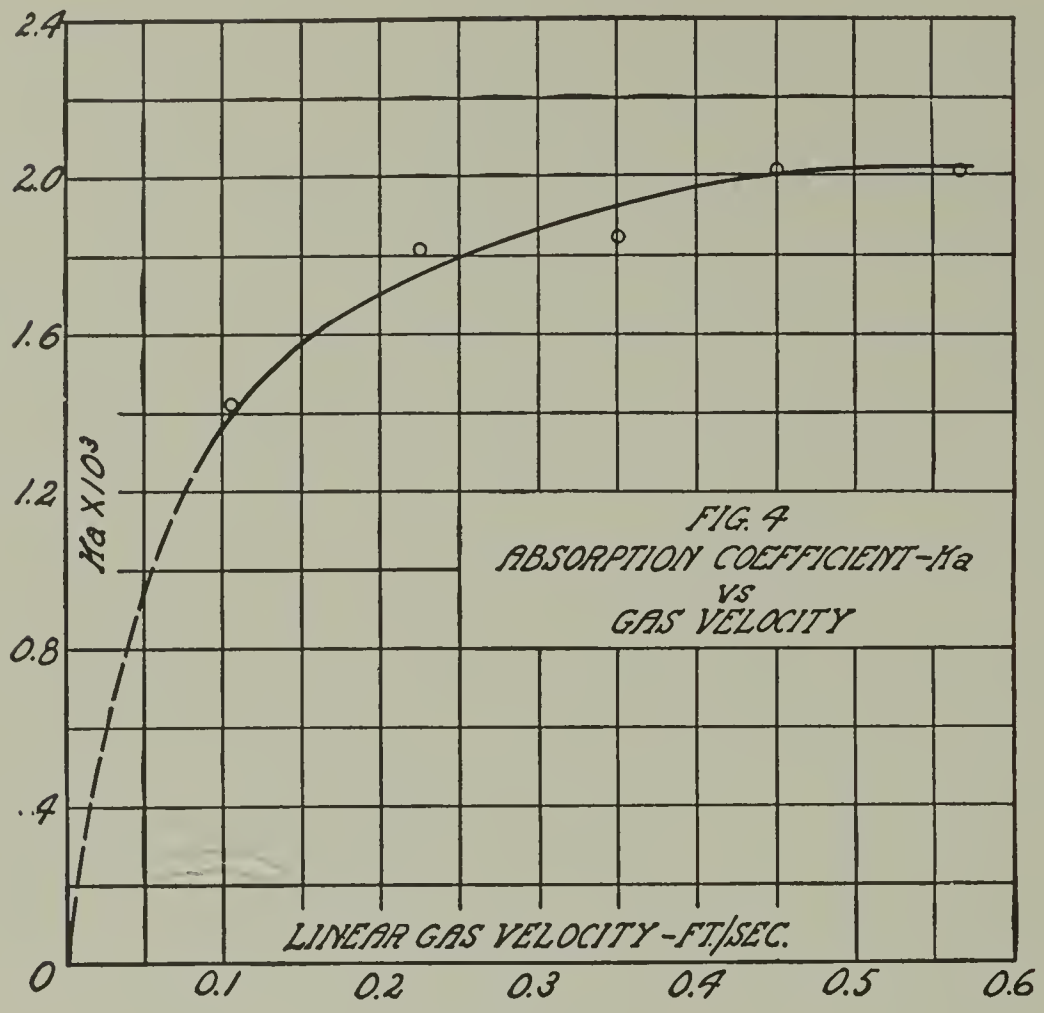


FIG. 4.

TABLE IV

EFFECT OF LINEAR GAS VELOCITY ON ABSORPTION

| Gas Velocity ft./sec. | $ka \times 10^3$ | Lbs. $SO_2$ Absorbed/min. $\frac{dW}{d\theta}$ | $\Delta P$ mm. Hg | Per Cent Absorption | Per Cent Equilibrium |
|---|---|---|---|---|---|
| 0.113 | 1.41 | 0.0256 | 20.8 | 92.0 | 15.8 |
| 0.223 | 1.81 | 0.0480 | 30.3 | 77.7 | 28.4 |
| 0.352 | 1.84 | 0.0627 | 39.0 | 61.1 | 35.0 |
| 0.449 | 2.06 | 0.0688 | 38.1 | 50.5 | 40.5 |
| 0.565 | 2.02 | 0.0694 | 39.4 | 47.7 | 40.2 |

*Series V* was made on an unpacked tower (same as in Series I) the water rate being 17.3 lbs. per sq. ft. per minute, with a gas velocity of 0.25 ft. per sec., the temperature being varied from 60° F to 120° F. The results are shown in Table V and in Fig. 5 is plotted *ka*, the absorption coefficient, versus temperature.

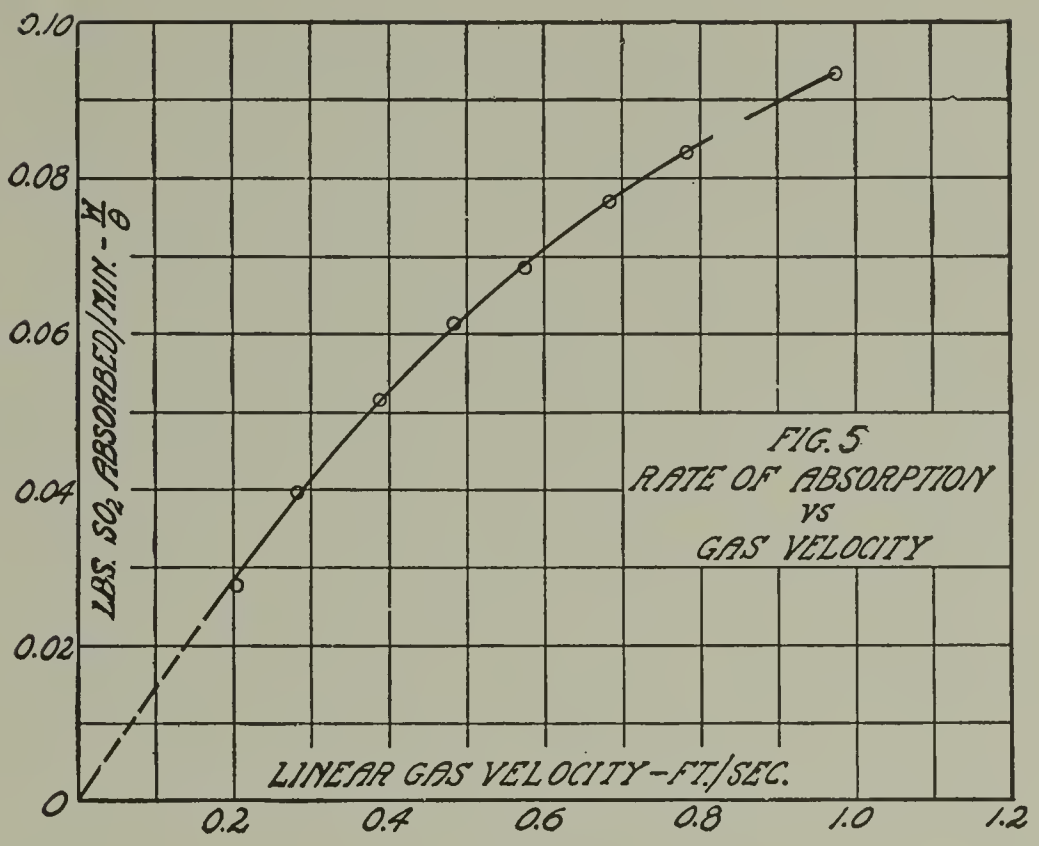


FIG. 5.

TABLE V

EFFECT OF TEMPERATURE ON ABSORPTION

| Temp. °F | $ka \times 10^3$ | Lbs. $SO_2$ Absorbed/min. $\frac{dW}{d\theta}$ | Per Cent $SO_2$ Absorbed | Per Cent Equilibrium Reached |
|---|---|---|---|---|
| 60 | 0.62 | 0.0241 | 29.1 | 27.5 |
| 80 | 0.56 | 0.0201 | 24.7 | 40.8 |
| 100 | 0.46 | 0.0162 | 18.4 | 48.2 |
| 120 | 0.42 | 0.0119 | 14.5 | 56.5 |

## DISCUSSION OF RESULTS

*The Effect of Gas Velocity.*—In all cases (Series I to IV and Figs. 1 to 4 inclusive) it will be seen that with an increase in gas velocity *ka* increases probably from zero (or a point near to it) at a rapid rate, the increase in *ka* growing less at the high gas velocities. Fig. 5 shows how the rate of absorption (lbs. $SO_2$ absorbed per minute, Series III) increases with gas velocity. This also is indicated in Fig. 6 which shows how the per cent equilibrium reached by the absorbing liquor increased from 15 per cent to 52 per cent with an increase in gas velocity from 0.2 ft. per sec. to 1.0 ft. per sec. However, the exit losses increase with gas velocity as shown in

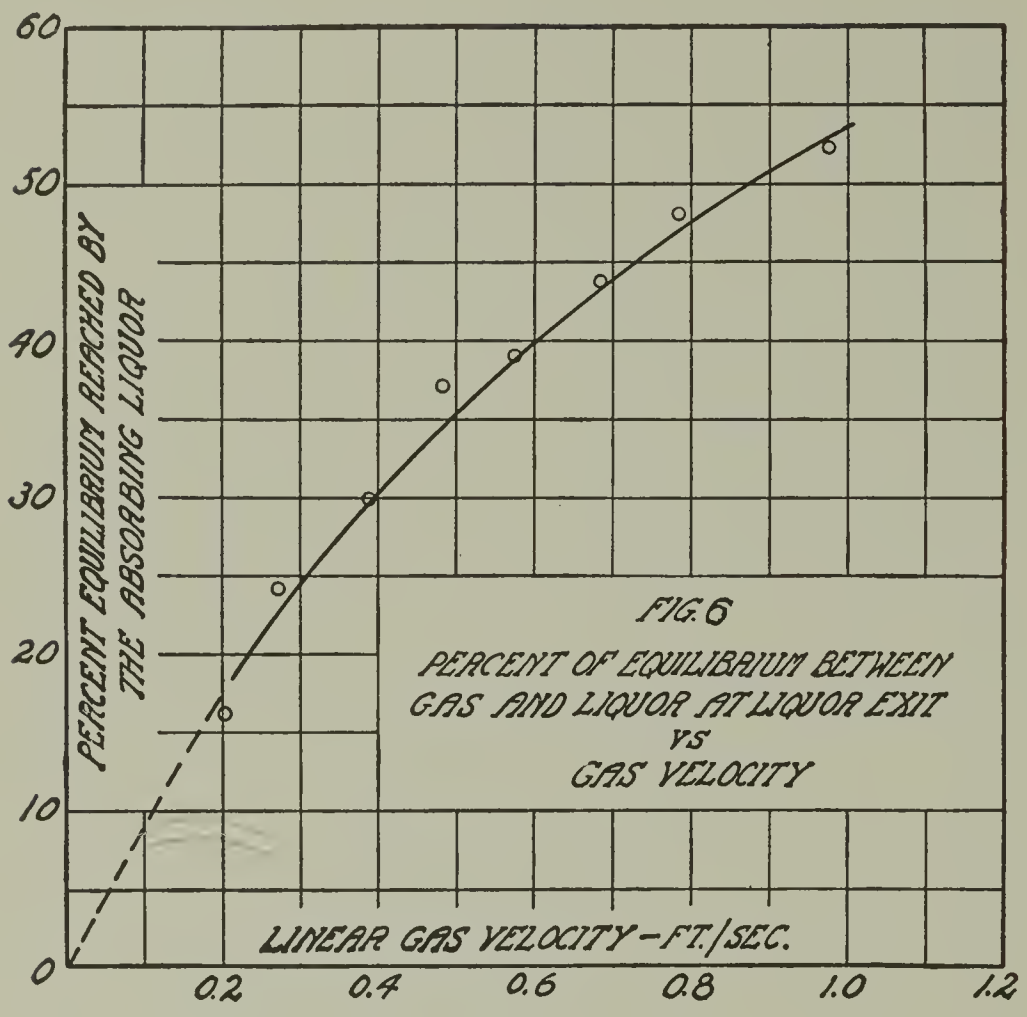
60
50
40
30
20
10
0
PERCENT EQUILIBRIUM REACHED BY THE ABSORBING LIQUOR
FIG. 6
PERCENT OF EQUILIBRIUM BETWEEN GAS AND LIQUOR AT LIQUOR EXIT VS GAS VELOCITY
LINEAR GAS VELOCITY - FT./SEC.
0.2
0.4
0.6
0.8
1.0
1.2

FIG. 6.

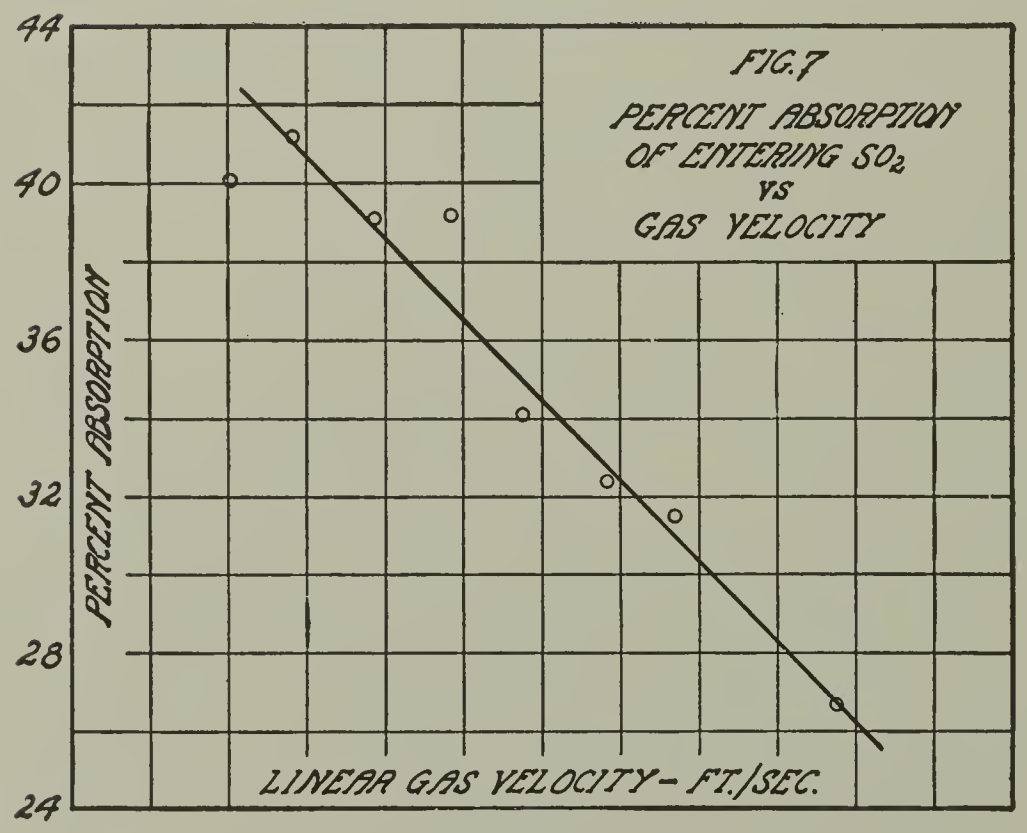
44
40
36
32
28
24
PERCENT ABSORPTION
FIG. 7
PERCENT ABSORPTION OF ENTERING $SO_2$ VS GAS VELOCITY
LINEAR GAS VELOCITY - FT./SEC.

FIG. 7.

Fig. 7, which gives the per cent absorption versus gas velocity.

In considering equation (2) for the transfer of heat through gas film it is seen that increased gas velocity increases the heat transfer through the gas film proportional to the mass velocity of the gas to the 0.8 power or in other words the *resistance* to the flow of heat decreases *inversely* as the velocity to the 0.8 power. Now if the resistance $1/ka$ to the transfer of $SO_2$ from the gas to the liquid is composed of a gas film and a liquid film, then:

$$\frac{1}{ka} = R_g + R_L$$

Assuming that the gas resistance varies inversely as the gas velocity and that gas velocity has no effect on the liquid film we have:

$$\frac{1}{ka} = \frac{C}{V^{0.8}} + R_L \qquad (5)$$

where $ka$ = absorption coefficient
$V$ = gas velocity
$R_L$ = liquid film resistance
$C$ = constant
$R_g$ = gas film resistance

Whitman and Keats [1] do not consider the liquid film to be unaffected by gas velocity, while C. S. Robinson [5] finds otherwise. Fig. 8 shows $1/ka$ plotted against $1/V^{0.8}$ for Series 1 to 4 inclusive, the points falling close to straight lines as one would expect if equation (5) is correct. Based on these assumptions, the relative liquid-film resistance and the gas-film resistance at different velocities were computed and the results are shown in Table VI.

TABLE VI

RELATIVE LIQUID AND GAS FILM RESISTANCES AT VARIOUS GAS VELOCITIES

| Series | Packing | Liquid Resistance | Gas Resistance, $R^g$, at | | |
|---|---|---|---|---|---|
| | | | Gas. Vel. of 0.1′ per sec. | Gas Vel. of 0.3′ per sec. | Gas Vel. of 0.5′ per sec. |
| 1 | Wall only wetted | 0.83 | 1.57 | 0.66 | 0.44 |
| 2 | Spray | 0.83 | 0.69 | 0.29 | 0.19 |
| 3 | 1 in. diam coke | 0.21 | 0.63 | 0.26 | 0.17 |
| 4 | Spiral tile | 0.40 | 0.33 | 0.14 | 0.10 |

The equations connecting the absorption coefficient, $ka$, expressed in lbs. per min. per cu. ft. of volume per mm. Hg partial pressure difference with gas velocity, $V$, in ft. per sec. are as follows:

| Series | Packing | Equation |
|---|---|---|
| 1 | Wetted wall | $\frac{1}{ka} = \frac{0.25}{V^{0.8}} + 0.83$ |
| 2 | Spray | $\frac{1}{ka} = \frac{0.11}{V^{0.8}} + 0.83$ |
| 3 | 1″ coke | $\frac{1}{ka} = \frac{0.10}{V^{0.8}} + 0.21$ |
| 4 | 3″ spiral tile | $\frac{1}{ka} = \frac{0.052}{V^{0.8}} + 0.40$ |

The first term on the right-hand side of the equations is the gas resistance term, while the second refers to the water resistance. In Series 2, 3, and 4 the water rate was constant at approximately 32 lbs. water per sq. ft. per min., while in Series 1 it was 17 lbs.

It is to be noted that the liquid-film resistance follows the order of magnitude one would expect, namely, that it is least with the 1 in. coke-packed tower and greatest with the spray and wetted-wall type of tower. The spiral-packed tower is intermediate in this respect between spray and the coke-filled towers. From an inspection of Table VI and Figs. 1 to 4 inclusive and Fig. 8 it can be said that the data show the effect of the two films, the effect of gas velocity at low gas velocities being great since the main resistance is the gas film, whereas at high gas velocities the effect is due to the increasing importance of the fairly constant liquid film. Furthermore, these data indicate why increased gas velocity has such a small effect on the absorption coefficient of spray type of towers, namely, that the liquid-film resistance which is fairly constant with increasing gas velocity is the major resistance, in addition to the gas resistance being excessively high due to "slippage" between the gas and liquid. This treatment shows quickly the line of attack along which to improve any given type of absorption tower; that is to say, for example, whether the liquid-film resistance should be lowered by increased water velocity or the gas-film resistance lowered by increased air velocity.

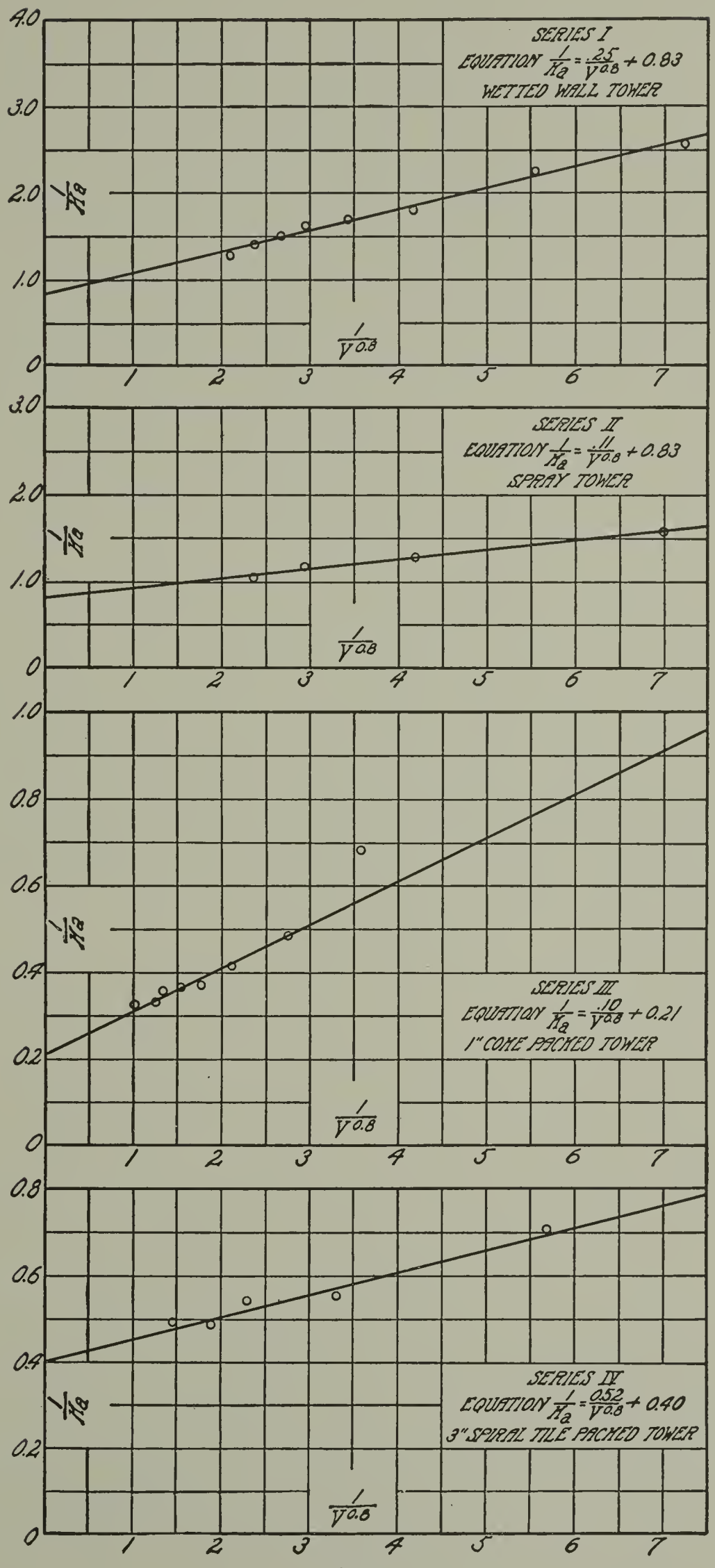
SERIES I
EQUATION $\frac{1}{K_a} = \frac{.25}{V^{0.8}} + 0.83$
WETTED WALL TOWER
SERIES II
EQUATION $\frac{1}{K_a} = \frac{.11}{V^{0.8}} + 0.83$
SPRAY TOWER
SERIES III
EQUATION $\frac{1}{K_a} = \frac{.10}{V^{0.8}} + 0.21$
1" COKE PACKED TOWER
SERIES IV
EQUATION $\frac{1}{K_a} = \frac{0.52}{V^{0.8}} + 0.40$
3" SPIRAL TILE PACKED TOWER
$\frac{1}{K_a}$
$\frac{1}{V^{0.8}}$

FIG. 8

FIG. 8.

## General Data

| Gas Velocity Feet per Sec.* | Cu. Ft. of Gas to Tower per Minute S't'd Cond.† | Per cent $SO_2$ in Entrance Gas | Per cent $SO_2$ in Exit Gas | Temp. Entrance Gas ° F. | Temp. Exit Gas ° F. | Pressure Entrance Gas In $H_2O$ | Pressure Exit Gas In $H_2O$ | Barometer Mm. Hg | Water Fed to Tower, c.c. per Sec. | Temp. Liquor | | Per cent $SO_2$ —Exit Liquor |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | Feed ° F. | Prod. ° F. | |

## Table I

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.84 | 2.22 | 7.5 | 4.1 | 58 | 57 | 0.4 | 0.25 | 758 | 43.2 | 57 | 56.5 | 0.227 |
| 0.125 | 2.98 | 7.5 | 4.6 | 59.5 | 58.5 | 0.7 | 0.6 | 766 | 46.0 | 58 | 58 | 0.266 |
| 0.166 | 3.96 | 7.4 | 4.9 | 60.5 | 58.5 | 1.2 | 1.0 | 758 | 46.0 | 58 | 58 | 0.333 |
| 0.213 | 5.05 | 7.3 | 5.1 | 60 | 57 | 1.6 | 1.2 | " | 44.2 | 57 | 56.5 | 0.355 |
| 0.256 | 5.57 | 7.4 | 5.3 | 61 | 57 | 2.5 | 1.6 | " | 44.0 | 57 | 57 | 0.377 |
| 0.294 | 6.95 | 7.8 | 5.9 | 63 | 57 | 3.4 | 1.8 | " | 43.8 | 57 | 56.5 | 0.433 |
| 0.339 | 8.40 | 7.8 | 6.0 | 64 | 58 | 4.6 | 2.8 | " | 43.6 | 56 | 56.5 | 0.463 |
| 0.396 | 12.7 | 7.4 | 6.2 | 66 | 59 | 6.3 | 3.8 | " | 43.4 | 57 | 56.5 | 0.495 |

## Table II

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.088 | 20 | 9.1 | 3.1 | 55.5 | 53.5 | 4.0 | 2.5 | 775 | 32.6 | 53 | 54 | 0.52 |
| 0.167 | 4.2 | 8.3 | 4.4 | 56 | 53.5 | 1.2 | 0.75 | " | " | 55 | 55 | 0.70 |
| 0.254 | 7.3 | 8.7 | 5.9 | 56 | 54.5 | 2.2 | 1.6 | " | " | 55 | 55 | 0.88 |
| 0.341 | 9.3 | 8.8 | 6.3 | 57 | 53.5 | 3.8 | 3.0 | " | " | 55 | 56 | 1.01 |

## Table III

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.204 | 4.5 | 8.6 | 0.7 | 57 | 55 | 0.2 | 0.2 | 762 | 84.3 | 53.5 | 53.5 | 0.249 |
| 0.282 | 6.2 | 8.7 | 0.8 | 58 | 58 | 0.45 | 0.35 | " | " | " | " | 0.356 |
| 0.389 | 8.5 | 8.6 | 1.2 | 58 | 56 | 0.85 | 0.65 | " | " | " | " | 0.462 |
| 0.484 | 10.7 | 8.2 | 1.7 | 59 | 56 | 1.5 | 1.0 | " | " | " | " | 0.548 |
| 0.578 | 12.8 | 8.8 | 2.3 | 59 | 54 | 1.95 | 1.3 | " | " | " | " | 0.613 |
| 0.684 | 15.1 | 8.8 | 3.0 | 59 | 55 | 2.25 | 2.0 | " | " | " | " | 0.685 |
| 0.785 | 17.4 | 8.5 | 3.1 | 60 | 54 | 3.5 | 2.6 | " | " | " | " | 0.74 |
| 0.976 | 22.3 | 8.8 | 4.1 | 62 | 54 | 5.7 | 4.5 | " | " | " | " | 0.83 |

## Table IV

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.113 | 1.95 | 8.0 | 0.7 | 57 | 57 | 0.2 | 0.15 | 757 | 85.3 | 55 | 55 | 0.225 |
| 0.223 | 3.9 | 8.8 | 2.1 | 60 | 57 | 0.9 | 0.7 | " | " | 55 | 55 | 0.424 |
| 0.352 | 6.4 | 9.0 | 3.7 | 60 | 55 | 2.0 | 1.5 | " | " | 55 | 56 | 0.553 |
| 0.449 | 9.0 | 8.5 | 4.4 | 64 | 56 | 3.6 | 2.8 | " | " | 56 | 56 | 0.606 |
| 0.565 | 9.5 | 8.6 | 4.7 | 65 | 55 | 5.9 | 4.7 | " | " | 56 | 56 | 0.610 |

## Table V

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.242 | 5.4 | 8.6 | 5.3 | 67 | 63 | 1.9 | 1.4 | 768 | 47.9 | 59 | 60 | 0.382 |
| 0.251 | 5.8 | 7.9 | 6.2 | 77 | 77 | 2.0 | 1.6 | " | 45.5 | 80 | 82 | 0.334 |
| 0.262 | 6.2 | 7.9 | 6.6 | 102 | 93 | 2.4 | 1.9 | " | 45.5 | 101 | 101 | 0.269 |
| 0.267 | 6.5 | 7.1 | 6.1 | 106 | 109 | 3.0 | 2.4 | " | 45.5 | 122 | 119 | 0.198 |

* Calculated from Orifice Data. † Calculated from Gas and Liquor Analyses.

It is of importance to note, that C. S. Robinson [5] finds the absorption coefficient *ka* of cooling towers to be linearly proportional to the air velocity, the line for *ka* versus air velocity passing through zero. As pointed out by Robinson [5] and Whitman and Keats [1] during adiabatic humidification or air cooling, the water temperature remains constant with the result that no liquid film exists, leaving only one film resistance, the gas film. Robinson's [5] data show that the gas-film resistance is inversely proportional to the gas velocity to the 0.8 power and that the liquid-film resistance, in the case mentioned, is zero.

*The Effect of Temperature.*—Series 5 and Fig. 9 show that *ka* goes down with increasing temperature, although from analogy with the flow of heat film coefficients one would expect it to inincrease, the gas film conductivity increasing with the square root of the absolute temperature and the liquid film conductivity increasing with the fluidity of the water. One would expect the amount of $SO_2$ absorbed per minute to decrease with rising temperature since the driving force $\Delta P$ falls, and this is actually the case (See columns 3 and 4, Table V). It is to be noted that at 60°F and a gas velocity of 0.25 ft. per sec. the total resistance ($1/ka$) is made up of the liquid-film resistance to the extent of 65 per cent of the total.

## Summary

1. The advisability of studying absorption by methods successfully used in the study of the similar and related field, flow of heat, is pointed out.

2. The effect of the two resistances, the "gas film" and the "liquid film," is shown by studying the effect of gas velocity on the absorption of $SO_2$ by water.

3. The gas-film resistance appears to be proportional to the gas velocity to the 0.8 power.

4. The liquid-film resistance appears to be practically independent of the gas velocity.

5. The overall coefficient of absorption rises rapidly with an increase in gas velocity, reaching an asymptote due to the comparatively stationary liquid-film resistance.

6. The equations connecting the rate of absorption with gas velocity are as follows:

| | |
|---|---|
| Wetted Wall Tower | $\frac{1}{ka} = \frac{0.25}{V^{0.8}} + 0.83$ |
| Spray Tower | $\frac{1}{ka} = \frac{0.11}{V^{0.8}} + 0.83$ |
| Coke Tower, 1″ Coke | $\frac{1}{ka} = \frac{0.10}{V^{0.8}} + 0.21$ |
| Spiral Tile Tower | $\frac{1}{ka} = \frac{0.052}{V^{0.8}} + 0.40$ |

7. The overall coefficient of absorption, $ka$, the driving force, and the lbs. of $SO_2$ absorbed per minute all decreased with an increase in temperature.

## Acknowledgment

The authors wish to thank M. B. Donald and C. W. Tyson students in the School of Chemical Engineering Practice, Massachusetts Institute of Technology, whose investigations are here discussed. Their thanks are also due to the Merrimac Chemical Company, South Wilmington, Mass., in whose plant this work was carried out.

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Department of Chemical Engineering,
Massachusetts Institute of Technology,
Cambridge, Mass.

## Discussion

Mr. Van Arsdel: I should like to ask Mr. Haslam if he has sufficient information from his experiments to answer whether any peak has been observed in the curve of the absorption coefficient versus gas-flow in any other case beside that of $SO_2$ and water?

Mr. Haslam: No, although we get that same peak in tests on two different towers.

Mr. Van Arsdel: That coincides with our experience in

$SO_2$, as I mentioned briefly in the paper a while ago, and it just happens in that case that the critical point corresponds numerically in flow ratio to the Henry constant; if that were true in the case of, say, ammonia and water, it would explain why you did not reach this maximum-point.

MR. HASLAM: The physical limitations of the equipment being tested prevented our reaching the critical point in the absorption of ammonia and water, but am I to understand that you got that same peak with $SO_2$?

MR. VAN ARSDEL: Yes.

MR. HASLAM: We did not expect it at first, and therefore we verified it with another kind of tower.

MR. VAN ARSDEL: We also got a similar peak in the curve of absorption-coefficient versus water-flow, as perhaps you did.

MR. HASLAM: Our work on water velocity indicates an increase in rate of absorption until we get to a critical velocity which completely wets the packing and after this velocity is reached we find no increase in the rate of absorption until we get to an extreme water rate (in the case of a coke packed tower). We did not reach any point where we got a decrease. Do I understand you got a decrease, with increase in water rate?

MR. VAN ARSDEL: Yes.

DR. WITHROW: I should like to ask if it might be possible that the explanation of that lower ratio which you express difficulty in explaining might lie in the solubility factor. As we know gases normally are less soluble in liquids, water in this case, the temperature is elevated.

MR. HASLAM: No, solubility or back pressure is taken care of in the driving force, and is allowed for. We expect on further work to find that the $ka$ is independent of solubility as well. Has Mr. Van Arsdel tried that out?

MR. VAN ARSDEL: The constant $k_2$ used in our work was independent of the solubility.

MR. HASLAM: If the effect of temperature were merely due to the back pressure of the $SO_2$ of the hot liquid, and that alone, it would be taken care of by the $\Delta P$.

MR. VAN ARSDEL: I might mention, though, that we found generally an increase in the transfer coefficient with increasing temperatures.

MR. HASLAM: You found that it increased?

MR. VAN ARSDEL: Yes, as nearly as we could tell it was inversely proportional to the viscosity of the liquid.

MR. HASLAM: Did you find that in $SO_2$?

MR. VAN ARSDEL: Yes we have tried only $SO_2$.

MR. HASLAM: Our other work on viscosity, where we artificially changed the viscosity of the liquor, indicated that the specific rate of absorption was inversely proportional to the viscosity, until we got more liquid adhering to the filling in the tower.

MR. VAN ARSDEL: In our theoretical work that viscosity relation was regarded as being accurately descriptive.

PRESIDENT HOWARD: Is there any further discussion? [No response.] If not, we will proceed to the next paper.

MR. VAN ARSDEL (communicated): Upon reflection I am not sure but that Dr. Withrow caught sight of the reason for this unexpected relation of transfer-coefficient to temperature, and that the solubility of the gas was not, in fact, eliminated from influence on the constant obtained by the authors. Their fundamental expression for the "driving-force" of absorption is $(P - \alpha x)$ where $\alpha = P/x$ at equilibrium; $\alpha$ is therefore the inverse of a solubility-constant. Now if the expression for "driving-force" were something like $[(P/\alpha) - x]$, experimental results at constant temperature would have been in equally good agreement, since $(P/\alpha) - x = (l/\alpha)(P - \alpha x)$; but when temperature changed, the constants obtained would differ by this solubility-factor, $l/\alpha$. This factor is in the right direction and very nearly in the right amount to eliminate the puzzling influence of temperature referred to in the discussion. For 20 per cent $SO_2$ Haslam, Ryan and Weber found $ka$ in a certain tower to be 0.00082 at 20° C. and 0.00057 at 40° C.; the solubility of $SO_2$ at 40° is 0.48 of its solubility at 20° (Landolt-Börnstein); dividing 0.00057 by 0.48, the "corrected" $ka$ for 40° is 0.00119. Now 0.00082 and 0.00119 come within 5 per cent of following the inverse-viscosity relationship which was expected. It may be pointed out that Donnan and Masson's expression for "driving-force" $(km - n)$, is equivalent to $(P/\alpha) - x$.

# A THEORY OF GAS ABSORPTION IN COUNTER CURRENT APPARATUS

By EDWIN M. BAKER

Read at the Wilmington, Del., Meeting, June 23, 1923

Problems involving the unit operation of gas absorption frequently arise in many fields of chemical engineering. These problems have long been solved by rule-of-thumb methods, though of late years the theory involved has received increased consideration by chemical engineers. The developments in this field have recently been carefully reviewed by W. B. Van Arsdel [1] who summarized the results, and advanced formulations free from many of the restrictive simplifying assumptions which characterized earlier papers.

It is my purpose in this paper to present a theory of gas absorption based on the conception of a gas absorption system composed of a series of units in each of which the liquid and gas which enter are brought into equilibrium, forming a new gas and a new liquid which flow from the system in opposite directions. These units will be designated as "equilibrium units" in this paper. These units may conveniently be first conceived of as belonging to a batch apparatus, represented diagramatically in Fig. 1.

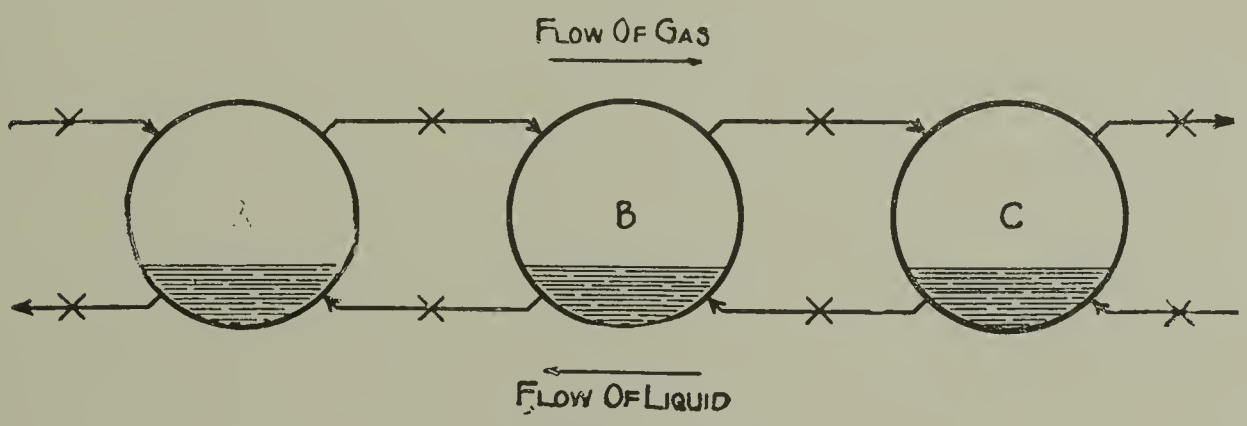


Fig. 1

This figure represents an ideal condition where the units are all the same size, and where the gas and liquid may be made to pass from one vessel to another, completely and instantaneously. *A*, *B*,

[1] *Trans. Amer. Inst. Chem. Eng.*, **14**, 391–413 (1921–22). See also, *Chem. and Met. Eng.*, **20**, 889–92 (1923).

and *C* are the containers into which gas and liquid may be introduced, and brought into equilibrium. Valves are provided in the gas and liquid lines connected to each receiver or unit. If the valves to each side of the units, *A*, *B*, and *C* are opened, the gas which was in A may be transferred completely into *B*, that which was in *B*, may be transferred into *C*, and so on. Likewise, the liquid which was in *C* may be transferred completely into *B*, that which was in *B* may be transferred into *A*, and so on. The relative amounts of gas and liquid in the units, and which are thus completely transferred, would be determined by the conditions of operation of the system. The liquid and gas which left the unit *A* would be in equilibrium. The same statement would hold true for the units *B* and *C*. The gas and liquid which entered *A*, *B*, and *C*, however, would not be in equilibrium at the moment of entry. The gas which enters *B* comes from *A* and the liquid entering *B* comes from *C*. If after the valves are closed, the gas and liquid commingle within each unit, on the further passage of time they will come to equilibrium. Then the valves may be opened allowing flow of liquid and gas again to take place, and thus on repeating the operation, a second quantity of liquid and gas are brought into equilibrium in each unit. In each of the units operating as a batch apparatus, the composition and temperature of the new gas and liquid formed in each unit will depend on the weights, compositions and temperatures of the gas and liquid entering the equilibrium unit, on the pressure, on the energy changes involved in processes taking place in the unit, and on the quantity of heat transferred between the unit and the environment. The quantity of change of composition of liquid and gas on approaching a single equilibrium of the type cited is definite, and is calculable if the above factors and the physical properties of the gases and liquid concerned are known.

In a gas absorption problem of the simplest sort, the gas phase consists only of absorbable gas, in which case only one equilibrium unit is required to produce a solution of the maximum concentration that may be obtained at the final temperature. This case hardly requires further consideration. Generally the gas phase consists of an inert or non-soluble gas, as well as absorbable gas. Two phases are involved, gas and liquid. If the gas phase consists of only one inert gas, a single absorbable gas, (and the vapors of the absorption liquid), and if a single absorption liquid is used, the

system consists of three components. Hence, by the Gibbs phase rule,

$$F = C + 2 - P$$
$$F = 3 + 2 - 2 = 3 \text{ degrees of freedom.}$$

The pressure in the apparatus will generally be fixed as one independent variable. Then, in addition to fixing the composition of the liquid phase, it is necessary to fix the temperature as an independent variable in order to fix the composition of the gas phase. It can be demonstrated that if the gas phase consists of more than one absorbable gas it is also necessary to fix pressure and temperature as independent variables in order to make the composition of the gas phase a dependent function of the composition of the liquid phase. It is of no moment that the concentration of the vapor of the absorption liquid in the gas phase can be substituted for temperature as an independent variable. The fact that the non-soluble portion of the gas phase may consist of two or more substances is also of no consequence so long as the total concentration stays constant since their relative concentrations will not be varied in the apparatus, and would not affect the operation if they were so varied. Such substances may therefore be properly treated as a single inert gas.

A number of equilibrium units may be connected in series so as to produce greater changes in compositions of liquid and gas than could be produced in a single equilibrium, the units being connected to permit countercurrent transfer of gas and liquid in the batch manner described. Fig. 2 may be taken as a representation of the

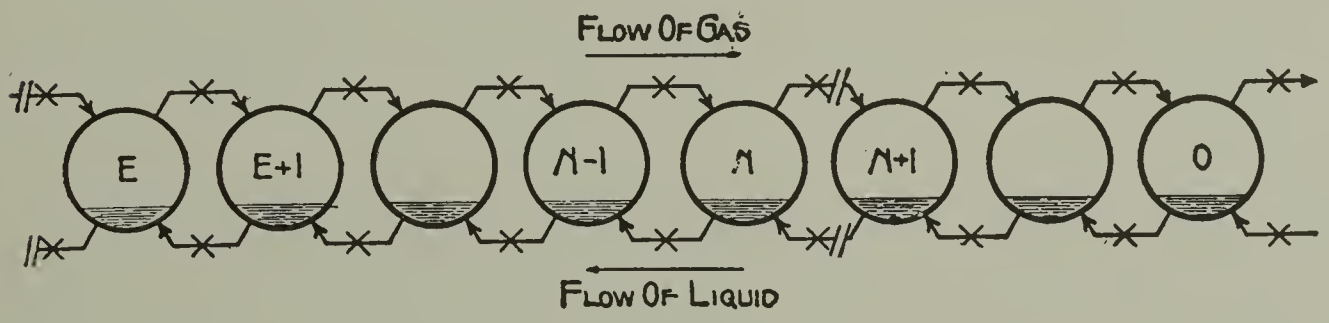


FIG. 2

apparatus, the number of units, however, may be greater than the number drawn. In referring to this arrangement of ideal batch units, the following nomenclature for a system concerned with only one absorbable gas, will be used.

$V$ = weight of inert gas in any unit of the system

$L$ = weight of pure absorption liquid in any unit of the system.

Thus, $\frac{V}{L}$ = the ratio of the weight of inert gas to the weight of pure absorption liquid in any unit.

For any specific unit, $V$ and $L$ should bear identical subscripts.

$C_V$ = composition of the gas phase, expressed as weight of absorbable gas per unit weight of inert gas.

$C_L$ = composition of the liquid phase, expressed as weight of absorbed gas per unit weight of pure absorption liquid.

Further subscripts are used to denote location in the apparatus, as follows:

Initial gas and initial liquid, $i$
Unit where *gas phase* enters system, $e$
Unit where *gas phase* goes *out* of system, $o$
Unit anywhere in the system, $n$

Units to each side of above units may be designated by subscripts, $n + 1$, $n + 2$, $n - 1$, the gas flowing from unit $n$ to units $n + 1$, $n + 2$, etc. Thus $V_i$ is the weight of inert gas entering the system; $V_i \cdot C_{Vi}$ is the weight of absorbable gas entering the system in the gas phase. Likewise, $V_e \cdot C_{Ve}$ is the weight of absorbable gas leaving the unit $e$, and entering unit $e + 1$ in the gas phase. Also, $C_{Ve}$ and $C_{Le}$ are equilibrium values as are also $C_{Vn}$ and $C_{Ln}$, etc. This nomenclature may at first seem involved, but inasmuch as most of the symbols are initials of the things represented, a little familiarity obviates necessity for recourse to the table of nomenclature.

The following equations have been derived by the simple process of striking balances of absorbable gas across properly selected portions of the apparatus. The process of transferring quantities of gas and liquid through the series of units in the manner described is assumed to go on continuously and regularly. In a continuous process, operating uniformly, the weights of each component entering and leaving any given system must be equal.[2] Thus since

[2] Many apparently complex problems can be readily solved by the application of this simple principle.

$V_i \cdot C_{Vi} + L_i \cdot C_{Li}$ = wt. of absorbable gas entering the system, and $L_e \cdot C_{Le} + V_o \cdot C_{Vo}$ = wt. of absorbable gas leaving the system, therefore,

$$V_i \cdot C_{Vi} + L_i \cdot C_{Li} = L_e \cdot C_{Le} + V_o \cdot C_{Vo} \tag{1}$$

and

$$L_i = \frac{L_e \cdot C_{Le} + V_o \cdot C_{Vo} - V_i \cdot C_{Vi}}{C_{Li}} \tag{2}$$

Equation (2), derived without any simplifying assumptions, gives the quantity of absorption liquid required for a weight $V_i$ of inert gas entering the system. The assumption that the weight of inert gas is constant at all points in the absorption system may usually be made. This must be true if there are no additions to or withdrawals of gases from intermediate parts of the apparatus. Also, in general the value of $L$ will be substantially constant at all points in the system. However, if there are no additions of liquid to intermediate parts of the system and no withdrawals of liquid from intermediate parts of the system, it does not necessarily follow that $L$ will be constant, as liquid may evaporate into the gas phase or be condensed from the gas phase into the liquid phase. The changes in the weight of pure absorption liquid from point to point in the apparatus are generally small and may be neglected without great error. Hence the case where these quantities are constant may properly be regarded as the general case, and the other condition as the special case.

Then $V_e = V_o = V_n = V_i = V$ and $L_e = L_o = L_n = L_i = L$ and these subscripts may conveniently be dropped when considering the general case.

Then, from equation (1)

$$V \cdot C_{Vi} + L.C_{Li} = L.C_{Le} + V.C_{Vo} \tag{3}$$

and,

$$L = V \frac{C_{Vi} - C_{Vo}}{C_{Le} - C_{Li}} \tag{4}$$

Equation (4) gives an expression for $L$ in terms of the weight of inert gas to be scrubbed, the initial composition of this gas, the concentrations of the liquid to be produced and that used for absorption, and the desired composition of the gas phase leaving the system.

If the gas phase leaving any unit $n$, has a partial pressure of absorbable gas greater by a finite amount than the vapor pressure of this gas from the liquid in the next unit, $n + 1$, then the change in composition of the liquid per perfect contacting unit will be finite. This change in composition of the liquid is called $\Delta C_L$ and is further defined by the equation

$$\Delta C_{Ln} = C_{Ln} - C_{Ln+1} \tag{5}$$

Thus $\Delta C_{Ln}$ is the increase in composition of the liquid on passing from the unit $n + 1$ to the next unit, $n$. It is not a constant, but is a variable since it is a function of the quantities $C_{Ln}$ and $C_{Ln+1}$.

The change taking place over the entire system may now be formulated by writing a balance of absorbable material over a portion of the apparatus, such as that between unit $n + 1$ and the end of the system where the gas enters, as indicated in Fig. 2. Equating weights of absorbable gas in the gas and liquid phases entering and leaving the portion of the system between the broken lines,

$$V.C_{Vi} + L.C_{Ln+1} = V.C_{Vn} + L.C_{Le} \tag{6}$$

Substituting the value of $C_{Ln+1}$ from equation (5) in equation (6)

$$V.C_{Vi} + L(C_{Ln} - \Delta C_{Ln}) = V.C_{Vn} + L.C_{Le} \tag{7}$$

Solving for $\Delta C_{Ln}$

$$\Delta C_{Ln} = \frac{V}{L}(C_{Vi} - C_{Vn}) - (C_{Le} - C_{Ln}) \tag{8}$$

This equation, expresses $\Delta C_{Ln}$ in terms of the composition of liquid in any unit at the moment of equilibrium, the equilibrium composition of vapor, the composition of gas entering the system, the ratio of inert gas to pure absorption liquid, and the composition of the liquid leaving the apparatus. This is the basic or fundamental equation, and its derivation has not involved any simplifying assumptions other than the constancy of $V$ and $L$. The ways in which $V$ and $L$ may vary have already been discussed.

Equation (8) may be used to calculate the number of equilibrium units that would be required in an ideal apparatus operating under given conditions. The quantities which must be known are:

The weight of inert gas to be treated, $V$
The weight of liquid used for absorption, $L$

The composition of the gas entering the system, $C_{Vi}$
The composition of the liquid entering the system, $C_{Li}$
The desired composition of gas leaving the system, $C_{Vo}$
The desired composition of liquid leaving the system, $C_{Le}$
The pressure in the system
The relationship between temperature and composition of the liquid phase.
The equilibrium concentrations of gas and liquid phases for all concentrations and temperatures of liquid encountered in the system

Given these data, the number of equilibrium units may be found by either of two methods;

(*a*) Calculation of the change in composition of liquid and gas phases in successive units, step by step.

(*b*) Calculation of the value of $\Delta C_L$ at several arbitrarily chosen values of $C_L$, and finding from these values the number of units required by integrating graphically the value of $\Delta C_L . f(C_L)$ between the limits of initial and final compositions of liquid.

These two methods will be illustrated in turn. For this purpose the following simplified problem on the absorption of carbon dioxide and gas in water will be worked. Gas saturated with water and analyzing by volume, on the dry basis, 40 per cent $CO_2$ gas and 60 per cent air at 25° C. is available for absorption. Water at 25° C. is to be used as the absorbing liquid and a solution containing 0.0005 grams of $CO_2$ per gram of water is to be produced. The concentration of $CO_2$ in the gas leaving the system is to be reduced to 5 per cent $CO_2$ by volume. The system is assumed to be so operated that the absorption is isothermal at 25° C. The pressure is assumed constant throughout the system at 760 mm. Under the given conditions the vapor pressure of water from the liquid phase will have a practically constant value of 23.7 mm. No great error is introduced, therefore, if the sum of the partial pressures of $CO_2$ and air in the gas phase is taken equal to $760 - 23.7 = 737.3$ mm. pressure. An allowance should be made for the weight of water absorbed in the whole apparatus, but for the sake of simplicity, further details of the interchange of water between the two phases will be neglected.

The first two columns of Table I give data taken from Findlay

and Williams [3] on the solubility of $CO_2$ in water at 25° C. Column I gives the concentration of the solution in grams of $CO_2$ per 100 grams of water. Column II gives the vapor pressure of $CO_2$ from solutions of the concentrations listed in Column I. Columns III and IV give corresponding derived values of $C_{Ln}$ and $C_{Vn}$. The values of $C_{Ln}$ in Column III are found by merely dividing the values of Column I by 100. The values of $C_{Vn}$ in Column IV are calculated from the values of Column II, Thus,

$$\frac{\text{Vapor pressure of } CO_2}{\text{Pressure of (air} + CO_2) - \text{Pressure of } CO_2} \times \frac{\text{density of } CO_2}{\text{density of dry air}} = C_{Vn}$$

or weight of $CO_2$ per unit weight of inert gas (air) in the gas phase. The pressure of air + $CO_2$ is the total pressure in the apparatus minus the pressure of water, and has been assumed constant at 737.3 mm. The relationship of $C_{Vn}$ and $C_{Ln}$ given in Columns III and IV of Table I, are plotted in Fig. 3. The abscissæ give values

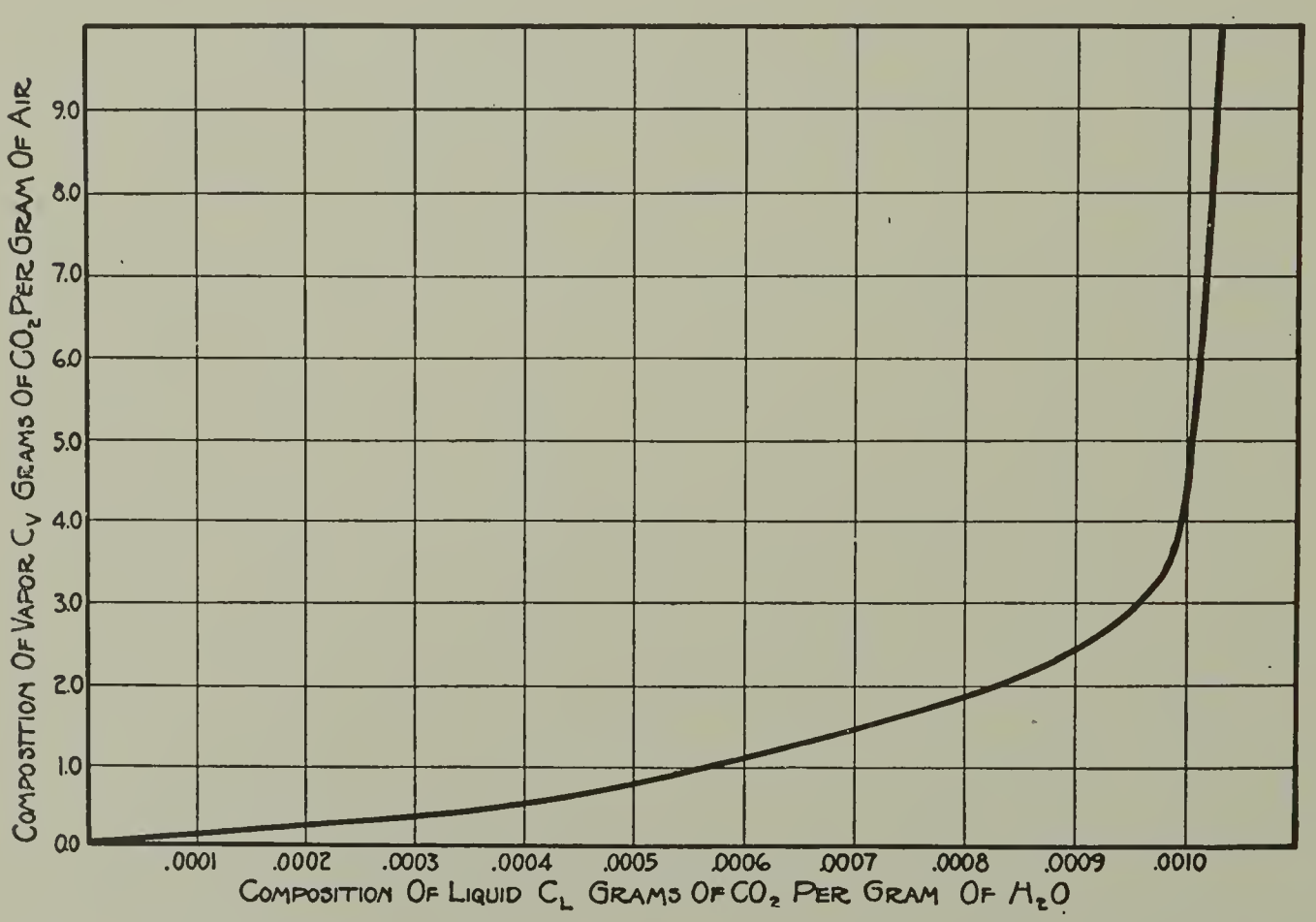


FIG. 3. Equilibrium Compositions of gas and liquid Phases System $CO_2$, air and water, 25° C and 760 mm. pressure.

[3] *J. Chem. Soc.*, 103–638 (1913).

TABLE I

SYSTEM CARBON DIOXIDE–WATER. EQUILIBRIUM CONCENTRATIONS OF GAS AND LIQUID PHASES AT 25° C.

| Conc. of Liquid g. $CO_2$ per 100 g. $H_2O$ | V. P. of $CO_2$ from Liquid | G. $CO_2$ per g. $H_2O$ $C_{Ln}$ | G. $CO_2$ per g. Air [4] $C_{Vn}$ |
|---|---|---|---|
| .0194 | 100 | .00019 | 0.24 |
| .0388 | 200 | .00039 | 0.57 |
| .058 | 300 | .00058 | 1.05 |
| .078 | 400 | .00078 | 1.81 |
| .097 | 500 | .00097 | 3.22 |
| .116 | 600 | .00116 | 6.67 |
| .136 | 700 | .00136 | 28.4 |
| .147 | 760 | .00147 | — |
| .155 | 800 | .00155 | — |

of $C_{Ln}$, and the ordinates give the corresponding equilibrium values of $C_{Vn}$ at 25° C.

The value of the ratio $V/L$ may be calculated by means of the relationship expressed by equation (4), from which

$$\frac{V}{L} = \frac{C_{Le} - C_{Li}}{C_{Vi} - C_{Vo}}$$

$C_{Vo}$ is the composition of the gas leaving the system, and since this is 5 per cent of $CO_2$ and 95 per cent air on the dry basis,

$$C_{Vo} = \frac{5}{100 - 5} \times \frac{\text{density of } CO_2}{\text{density of air}} = 0.082$$

$C_{Vi}$, the composition of the entering gas = 1.015.
Hence,

$$\frac{V}{L} = \frac{.0005 - 0.0}{1.015 - .082} = .000536$$

The successive values of $\Delta C_L$ in the various units may now be calculated from equation (8)

$$\Delta C_{Ln} = \frac{V}{L}(C_{Vi} - C_{Vn}) - (C_{Le} - C_{Ln})$$

The unit $e$ where the gas enters may for this illustration, and to prevent changing the subscripts, be considered as the unit $n$.

[4] At pressure of $CO_2$ + air = 737.3 mm.

Subsequent units in the system, in the direction of gas flow, will be designated as units $n + 1$, $n + 2$, etc. The composition of the liquid produced in this unit, $C_{Ln}$, is the composition of the final liquid, hence $C_{Ln} = 0.0005$. The ratio of $V/L$ has already been calculated. $C_{Vn}$ is the composition of gas in equilibrium with liquid of composition $C_{Ln}$. This value may be read from the curve of Fig. 3. Putting these quantities in the equation, the value of $\Delta C_{Ln}$ is found,

$$\Delta C_{Ln} = 0.000{,}536\ (1.015 - .830) - (.000{,}500 - .000{,}500)$$
$$\Delta C_{Ln} = 0.000{,}099$$

Equation (5) defining $\Delta C_{Ln} = C_{Ln} - C_{Ln+1}$, may now be used to calculate the composition of the liquid in the next unit, $n + 1$.

$$C_{Ln+1} = C_{Ln} - \Delta C_{Ln} = 0.000{,}500 - 0.000{,}099 = 0.000{,}401$$

This value of $C_{Ln+1}$ may now in like manner be used for calculating the change in composition of liquid produced in the next unit, since

$$\Delta C_{Ln+1} = \frac{V}{L}(C_{Vi} - C_{Vn+1}) - (C_{Le} - C_{Ln+1}), \text{ from equation (8)}$$

By proceeding in this way, calculations have been continued until a value for $C_V$ was obtained equal to $C_{Vo}$. The results of these calculations are given in Table II. Column I of this table gives the

TABLE II

DATA ON SOLUTION OF THE PROBLEM, METHOD (*a*)

| Unit | $C_L$ | $C_V$ | $\Delta C_L$ | $\frac{1}{\Delta C_L}$ |
|---|---|---|---|---|
| N | .000,500 | .830 | .000,099 | 10,100 |
| N + 1 | .000,401 | .601 | .000,123 | 8,130 |
| N + 2 | .000,278 | .380 | .000,118 | 8,470 |
| N + 3 | .000,160 | .200 | .000,097 | 10,310 |
| N + 4 | .000,063 | .079 | .000,063 | 15,900 |

unit referred to in subsequent columns. Column II gives the composition of liquid, $C_{Ln}$, $C_{Ln+1}$, etc. Column III gives the equilibrium composition of gas, $C_{Vn}$, $C_{Vn+1}$, etc. Column IV gives the corresponding calculated value of $\Delta C_{Ln}$, $\Delta C_{Ln+1}$, etc. Column V gives the reciprocal of $\Delta C_L$. The significance of this column of figures

will be discussed later. It is seen that five calculations and therefore five units are required to bring the composition of gas, $C_{Vn+4}$ to the value of $C_{Vo}$, which is the specified composition of gas leaving the system. The number of units required is therefore five units.

The method of calculation of the number of units is quite satisfactory if the number of units is small, but would be very tedious if the number were large. For this case, the method (*b*) previously mentioned, may be used. This method differs from method (*a*) only in that a few values of $C_{Ln}$ are chosen for the calculation of $\Delta C_{Ln}$, and the number of units required are then found by plotting the calculated data and graphically integrating.

The results of such calculations are given in Table III. Column I

TABLE III

DATA ON SOLUTION OF THE PROBLEM METHOD (*a*)

| $C_{Ln}$ | $C_{Vn}$ | $\Delta C_{Ln}$ | $\frac{1}{\Delta C_{Ln}}$ |
|---|---|---|---|
| .000,500 | .830 | .000,099 | 10,100 |
| .000,400 | .600 | .000,122 | 8,200 |
| .000,300 | .415 | .000,121 | 8,260 |
| .000,200 | .255 | .000,107 | 9,350 |
| .000,100 | .120 | .000,080 | 12,500 |
| .000,070 | .082 | .000,070 | 14,280 |

of this table gives the assumed values of $C_{Ln}$, column II corresponding equilibrium values of $C_{Vn}$ read from Fig. 3, column III the calculated values of $\Delta C_{Ln}$, and column IV the reciprocals of the values of $\Delta C_{Ln}$.

By definition, $\Delta C_{Ln}$, is the difference in composition of the liquid in two adjacent units, $n$ and $n + 1$, and is a variable depending for its value on the composition of the liquid in the unit $n$, as well as on other factors. However, if $C_{Ln}$ had a constant value then $1/\Delta C_{Ln}$ would be the number of equilibrium units required to increase the composition of the liquid by an amount equal to unit weight of absorbed gas per unit weight of pure absorption liquid, or to make $C_{Lf} - C_{Li} = 1.0$, where $C_{Lf}$ is the composition of the liquid leaving the group of units, and $C_{Li}$ the composition of liquid entering.

The reciprocal of $\Delta C_{Ln}$ does not give the number of units required to make this change of composition of liquid at a definite value of composition of liquid. Instead, it gives the average number of

units required to make a change of 1 (viz. $C_{Lf} - C_{Li} = 1$), in the composition of liquid, if the change in composition of liquid were to continue to take place uniformly, at the same rate as the average rate of change of composition of liquid between the points where the composition of the liquid is $C_{Ln}$ and $C_{Ln+1}$. This is illustrated in Fig. 4, using the data of Table II. Fig. 4 is a graph having as

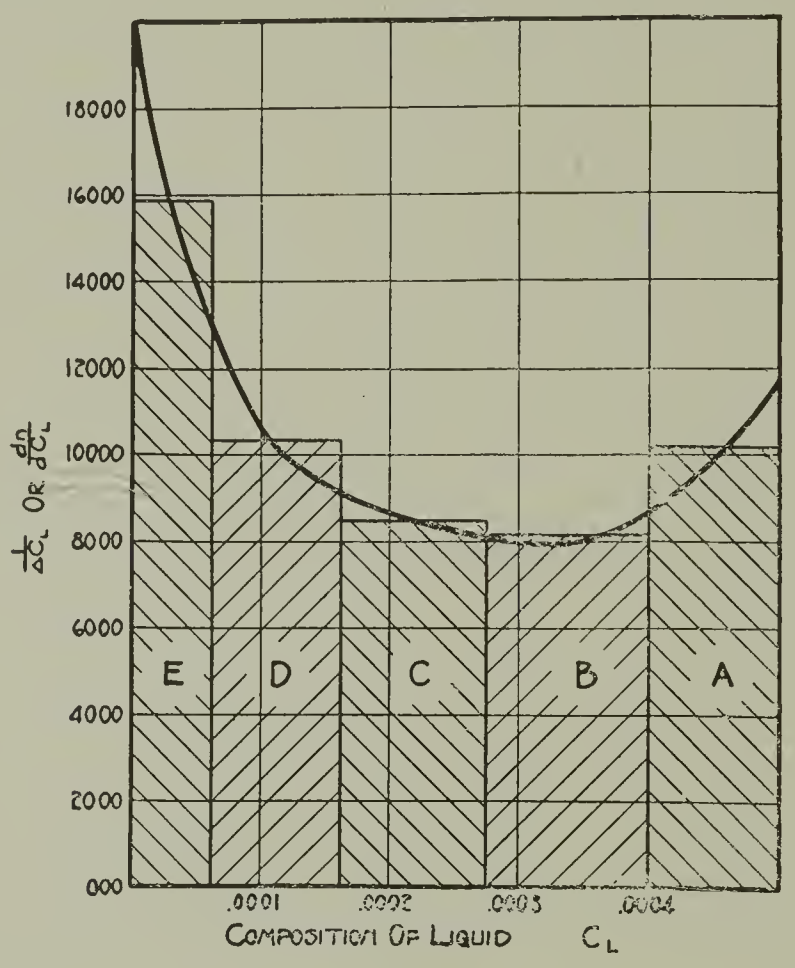


FIG. 4.

ordinates the value of the reciprocal of $\Delta C_L$, and as abscissæ composition of liquid.

The graph consists of five rectangles. The ordinate of the rectangle A is 10100, which is the average number of units that would be required, as stated above, to produce unit change in composition of liquid, if the rate of change continued to be the same as the average rate between the points where the composition of the liquid is 0.000,500 and 0.000,401. The values 0.000,500 and 0.000,401 are therefore established as the abscissæ of the rectangle. The other rectangles have been drawn in a like manner. If a smooth curve be now drawn so that the area under the curve between the abscissæ of any rectangle is the same as the area of the rectangle, then the ordinate of this curve gives the number of units required to make

unit change of composition of liquid, at the point where the liquid has the composition indicated by the abscissæ corresponding to this ordinate. The smooth curve thus drawn gives the average number of units required to make unit change of liquid composition, as a function of liquid composition at any point. If $n$ represents numbers of units, the ordinate of the curve may be expressed as $dn/dC_L$, or the reciprocal of the rate of change of liquid composition with respect to numbers of equilibrium units. The area under the curve between two compositions, $C_{Lf}$ and $C_{Li}$ is equal to

$$\int dn = \int_{C_{Li}}^{C_{Lf}} dC_L \cdot f(C_L)$$

Since the equation of the curve is not generally known, it is most convenient to integrate the right hand member by graphically computing the area under the curve between the abscissæ $C_{Lf}$ and $C_{Li}$. This integral is equal to $\int dn = n$, or number of units required to change the composition of liquid from $C_{Li}$ to $C_{Lf}$.

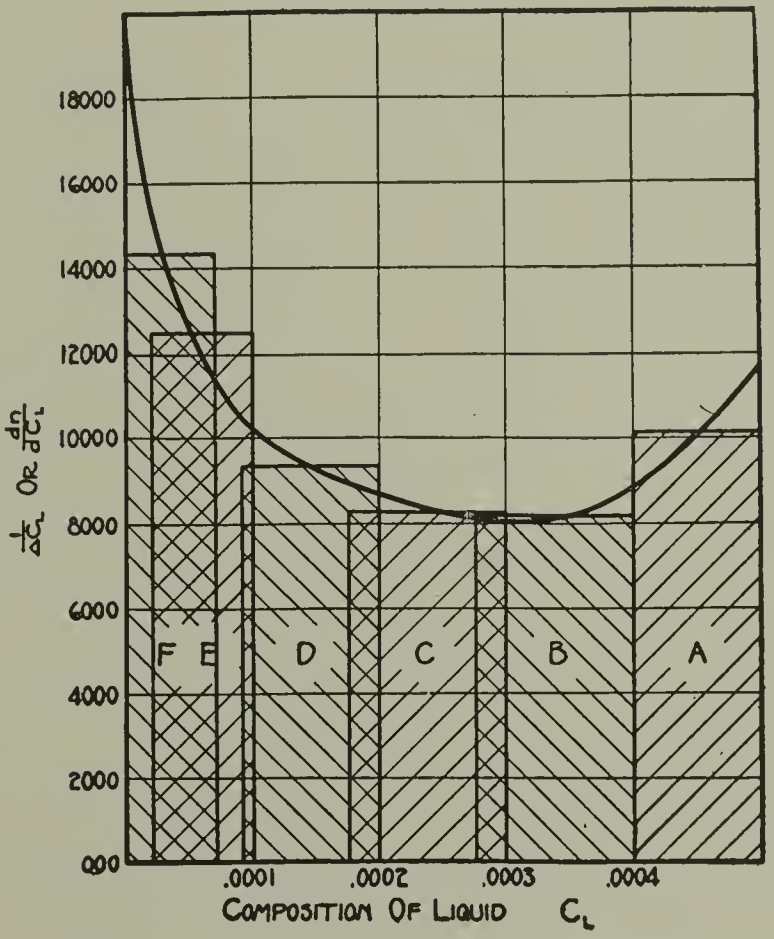


FIG. 5.

There is, of course, no point in actually carrying out this work where the method (*a*) of computing the number of units required

is used. Thus, in the example cited, the number of units required was known to be 5 units. When method (*b*) is used the situation is different, for the change of composition of liquid has not been computed unit by unit. Data such as that given in Table III is obtained by method (*b*) from which some rectangles can be plotted, as in Fig. 5, using again $1/\Delta C_L$ as ordinate and the two corresponding compositions of liquid as abscissæ. These rectangles serve as guides for drawing the smooth curve which expresses $dn/dC_L$ as a function of $C_L$. It is immaterial whether the rectangles overlap, or have spaces between, so long as sufficient rectangles are calculated to establish the locus of the smooth curve. Having the smooth curve, the area under the curve between the abscissæ $C_{Lf}$ and $C_{Li}$ may be graphically integrated. This area is the number of units required under the given conditions to change the composition of liquid from the initial to the final composition. This integral has been found for method (*b*), using the data of Table III, as shown in Fig. 5. The area under the smooth curve, between the abscissæ

$$C_{Li} = 0.0, \text{ and } C_{Lf} = 0.000{,}500 = 4.95$$

units, which checks method (*a*).

It should be noted that while this graphic integral does not take into consideration many of the factors affecting the rate of reaction or solution of the gas, it does define the number of equilibrium units necessary to make the required change in composition of gas and liquid under the conditions given, and therefore takes into account the "degree of unsaturation of the liquid." [5] That is, the calculation of the value of $\Delta C_L$ involves the factor of the difference in pressures of the absorbable gas in the two phases through the use of actual and equilibrium concentrations of gas and liquid. This difference in pressures is the driving force which causes the absorp- to take place, and the integral therefore takes into account this factor, which is of importance in determining the rate of absorption. The temperature of the system, either constant or variable, is also taken into account in part in that temperature determines the equilibrium values selected for the equilibrium compositions of liquid and gas in various parts of the system. Temperature is not taken into account in the sense that it would affect molecular mobility, and therefore viscosity and diffusion velocity, both of which affect the rate of gas absorption.

[5] Donnon and Masson, *J. Soc. Chem. Ind.*, 39, 236T (1920).

When the system treats a gas phase containing more than one absorbable gas, these gases may each be handled by the formulæ given. When the absorption (and evolution if any) of all absorbable gases and the vapor of the pure absorption liquid, as well as transfer of heat energy to or from the environment are taken into consideration, the sum of the energies of all sorts entering and leaving any portion of the system must be equal. If no energy is transferred to or from the surroundings, the changes must be adiabatic in nature. On the other hand, the changes may be purely isothermal if just the proper quantities of energy are transferred. Neither of these cases is common in practice. Some heat is usually transferred to the environment, but not a sufficient amount to make the reactions isothermal.

If the flow of gas and liquid between the units were continuous, instead of the ideal batch process described, the apparatus composed of a series of equilibrium units would be in its major aspects quite similar to a tourill system such as is commonly used in the absorption of hydrochloric acid. There are in fact but two points of difference, first, the one just noted of continuous versus discontinuous flow, and second, the fact that equilibrium of the phases is not attained in the tourill. If the flow of gas and liquid in the ideal batch process occurs frequently and at regular intervals, the process would in effect constitute continuous flow, especially if the quantities transferred at one time were made very small and the frequency of transfer made correspondingly great. No different result would be obtained if only a portion of liquid and gas in the units were transferred at a time, if the flow ratio, $V/L$ were not disturbed. Hence there is no fundamental difference in the two systems in the first respect.

While presumably no tourill will be built that brings about equilibrium between liquid and gas which flow through it at an appreciable velocity, nevertheless some number, not necessarily integral, of tourills treating gas and liquid in countercurrent flow may produce the same change in composition of liquid as that attained in one equilibrium unit. This number of tourills, under the given conditions, would therefore be in effect the equivalent of one equilibrium unit. For instance, in the example calculated for the absorption of $CO_2$ in which 5 equilibrium units were required, if 20 tourills operating under the given conditions produced a finished liquid and an exit gas of the given compositions, then 4

tourills would be the equilvalent of one equilibrium unit. Further, by finding the conditions under which any system of tourills is operating, and then calculating the number of equilibrium units required to do the same work under the given conditions, the effectiveness of the tourills may be expressed in terms of number of tourills equivalent to one equilibrium unit under the given conditions. It should be noted in this connection that the equations derived are applied to the ideal system, not the working system; and that it is the number of units, in the actual and ideal systems which accomplish the same work, which is compared. If it is desired to extend the actual system to accomplish more work, the number of equilibrium units required in the ideal system to do this additional work may be calculated. From the rating of the number of tourills in the system being operated which are equivalent to one equilibrium unit, the number of tourills to be added can be readily calculated with a fair degree of accuracy, since the conditions affecting the equivalence of tourills and equilibrium units will be substantially unchanged.

This method of comparing an actual system to the ideal system of equilibrium units may be further extended to include absorption columns. Flow of liquid and gas is continuous in the column, but flow of liquid and gas in the ideal batch system has been shown to be in effect continuous. A plate or bubbler cap column is composed of a series of units, just as is a tourill system, and therefore some number of plates may be the equivalent, in work done, of one equilibrium unit. A packed column is not composed of definite units, yet some number of feet of length of packed column may, in work done, also be the equivalent of one equilibrium unit, in the same manner that a number of tourills or tower plates may be the equivalent of one equilibrium unit. The formulæ derived are applied to the number of equilibrium units required for the ideal column, and the length of actual column accomplishing the same work is compared to the number of units required in the ideal system. The equations are not applied to the actual or working column.

A similar conception of a "theoretical plate," [6] or "perfect contacting unit," [7] has been used to advance the theory of distillation. Peters [8] in this way compared the effectiveness of different

[6] W. K. Lewis, *J. Ind. Eng. Chem.*, 14, 492–7 (1922).
[7] E. H. Leslie, "Motor Fuels," pp. 85–114.
[8] *J. Ind. Eng. Chem.*, 14, 476–9 (1922).

sizes of Rashig rings in rectification towers on the basis of "height of packing equivalent to one theoretical plate."

The expression in physical units of the amount of actual absorption media, number of tourills or feet of packed tower, which are the equivalent of one equilibrium unit, however, is no easy task, for the quantity is a variable, depending for its value on such factors as the velocity of liquid and gas, the intimacy and vigor of contact of liquid and gas; and the rate of diffusion of the absorbable gas through the gas phase, the boundary layers between gas and liquid, and through the liquid phase. The latter depends on the nature of the substances, on the temperature, pressure, the average distance through which diffusion must proceed which in turn depends on the agitation within the phases, thickness of the intermediate layer and perhaps numerous other factors. In this connection the mathematical treatment of the rate of diffusion in the related phenomenon of drying, by W. K. Lewis [9] is of great interest.

It seems to the writer that if ratings of various tower packings, tourills, and other absorption media were reported in the literature in terms of amount of absorption media that were equivalent to one equilibrium unit, under specified conditions of operation, a definite step would be taken in the direction of building up data on which absorption apparatus might be designed, and to which the performance of existing apparatus might be compared. Formulations permitting the general comparison of such data irrespective of the particular conditions would then have special value.

A bibliography of references on the theory and practice of gas absorption is given below.

## Acknowledgment

Acknowledgement is made of the valuable assistance of Professor Alfred H. White [10] in the preparation of this paper.

Department of Chemical Engineering,
University of Michigan

## Discussion

Mr. Peters: I should like to ask Mr. Baker if he has any idea of the dimensions of the equilibrium unit. The theoretical plate which he referred to runs about one foot in height for the average packing.

[9] *J. Ind. and Eng. Chem.*, 13, 423–8 (1921).

[10] Head of the Department of Chemical Engineering, University of Michigan.

MR. BAKER: I did not give any definite height for an equilibrium unit as I have no exact experimental data. While I have not been able to carry out experimental work as yet I may say that the height of an equilibrium unit would be the same as that of one theoretical plate.

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# THE RATE OF ABSORPTION OF HYDROCHLORIC ACID GAS IN THE TYLER VITREOSIL SYSTEM

By H. E. FRITZ and JAMES R. WITHROW

Read and discussed at the Wilmington, Del., Meeting, June 23, 1923

## Significance of the Work

The absorption of hydrochloric acid gas from admixture with air or other gases, or from practically pure gas itself, is a reasonably frequent chemical engineering problem. A knowledge of the rate of absorption, by water, of hydrochloric acid gas from a flowing stream of gases is fundamental to the intelligent design of absorption units. Nevertheless, there are no chemical engineering data extant. Those who may have investigated the problem have either answered their immediate question by "cut and try" or by estimation based upon a previous unit's experience, or if they actually determined the rate of absorption per square foot of absorption surface per hour they have not yet given it much publicity. The most recent handbooks of chemical engineering do not even mention this important engineering operation.

## Synopsis of this Report

The work covered in this report was an investigation of the absorbing power of a full-sized, fused quartz or "Vitreosil" absorption train designed on the Tyler system. The absorption was studied from the standpoint of constant make, or production, of acid of a desired concentration, in as small an absorption area as possible. No effort was made to find the maximum capacity of the system. Full load studies will be conducted when we have added an efficient scrubbing system after the experience gained in the study of light loads.

The data presented show:

(1) Pounds and cubic feet of hydrogen chlorid gas absorbed per square foot of absorbing area per hour, under certain conditions.

(2) Pounds of acid produced per square foot of absorbing area per hour, under certain conditions.

(3) Absorption area utilized in producing desired quantity of strong acid (1.175 sp. gr. (21.6° Beaumé) at 20° C.), under certain conditions.

The findings are arranged in tables and in the form of curve sheets.

A drawing showing the set-up with the necessary explanation is included.

## The Problem

We have initiated in this laboratory a comprehensive study of hydrochloric acid gas absorption. The available results are published at this time because of inquiry regarding, and visits to, our operating set-up, by engineers and operators who desired confirmation of experience or estimate. The work is being continued from various points of view and under conditions still closer to common muriatic plant conditions. In the meanwhile it is hoped that this paper will draw out some of the experience of operators of hydrochloric acid absorption systems.

Hydrochloric acid gas is generally absorbed for the production of the muriatic acid of commerce. Sometimes, however, the problem is the cleaning of an effluent gas. The gas is often the determinate product of a reaction, as in the manufacture of hydrochloric acid from salt or the combustion of hydrogen and chlorine. At other times the gas is the by-product of the chlorination of a hydrocarbon. The nature of the absorption problem varies materially in these different cases. It varies in the several ways of conducting even the standard salt-sulphuric acid reaction, and also at different times in this reaction as carried out in a muriatic acid plant.

To chemical engineers the absorption capacity of various types of absorbing systems for the manufacture of hydrochloric acid is generally an unknown factor. This is so much the case that few engineers and builders of these systems are able to design plants with any degree of precision.

The aim of this paper is to set forth the absorption data, obtained in perhaps the most modern system, in such form that they can be applied to the construction and operation of these units with a high degree of certainty.

The work was so planned as to determine the simplest conditions under which data could be obtained and presented at this time, thus enabling us to determine the additional arrangements

which will be required under our conditions adequately to handle studies under high velocities and various tail gas concentration to give maximum absorption rates.

Our work began with the study of low gas velocities and constant acid make. Maximum capacity investigations will follow.

Inasmuch as the concentration of hydrogen chloride usually varies over wide limits in differently designed acid plants, our plan purposed the collection of data on various concentrations of gas, starting with one hundred per cent concentration and grading off to one or two per cent by volume.

In this report we go only as low as thirteen per cent, which is the minimum limit of our system as at present arranged. Our next set-up will include a scrubbing tower and be further arranged to investigate the lower gas concentrations.

## Equipment and Operation

The equipment utilized in this work consists entirely of fused quartz or "Vitreosil" ware, and is one full-sized unit, set up in typical industrial fashion, so that the findings in the following pages should represent those which may be expected in actual operating practice, provided the operating factors fall within the limits of those in this work. Fig. 1 shows the "Vitreosil" absorption system set-up from whose operation the data were obtained. For our purpose it sufficed to generate hydrochloric acid gas by heating a mixture of muriatic acid and 66° sulphuric acid, diluting with air when desired.

The glass bottles shown at *A* in the side elevation serve as supply reservoirs, from which small pulsometers deliver the sulphuric and muriatic acids to the constant level acid feeds *B* (any excess returning to *A* through overflow lines), which serve as splash boxes for the pulsometers, the splash boxes exhausting through openings in the top as shown. From *B* the acid flows by gravity through calibrated nozzles into the generator *C*, which is partially submerged in the heating bath *D*. The contents of the generator are maintained at the desired temperature by the application of heat from the ring burner as shown below the bath.

As the acids flow into the generator dehydration of the muriatic acid takes place, and the liberated acid vapor passes upward through the straight pipe *E*, through the return bend and atmospheric cooler *F*, then the *U* trap (equipped with acid delivery) and into the

absorption vessels *V*. The entire system is maintained under a slight suction by means of the bronze ejector *H*. Distilled water is fed into the system at the bell end of the last vessel near *H*, at such a rate that the desired concentration of acid flows out the acid delivery of the "U" trap. It is therefore evident that the system is essentially counter-current in principle. Cooling water is allowed to flow over the outside of the vessels to remove the heat of absorption.

Special provision has been made in the set-up for sampling both acid and gases, as well as for taking temperature readings, on each vessel near the spigot end, also on the "U" trap and stoneware generator *C*.

The dimensions of the absorbing area of each vessel are approximately 11 x 30 inches, making a total of 3.05 square feet per vessel. Details of the system of which our set-up was a replica, as far as the parts actually used by us were concerned, need not be given here. They have already been published by Tyler.[1]

The generator is provided with a bleed line, just above the sides of the heating bath, to withdraw the spent acid and permit continuous operation, also an air line to dilute the gas at will with free air.

The rate of flow of both input feed water and acid gas were so arranged as to yield a finished acid of nearly constant gravity. The vessels were numbered in order, beginning with the lower marked number "one," going to the top, which was number "four."

## Procedure for Data Collection

All data submitted herein are based entirely upon the analysis of gases and finished acid.

The gas concentrations were determined by drawing a known volume from the point desired and absorbing the acid vapors in caustic soda solution. The diminution in volume being equivalent to the amount of acid vapor, therefore, if one hundred parts are drawn, the diminution will represent the gas content in percentage by volume.

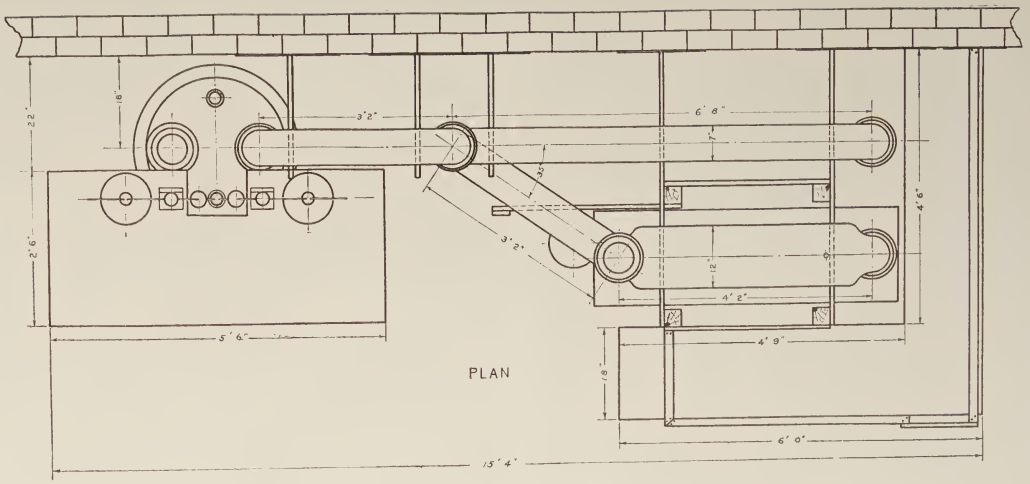
It should be noted, in connection with the gas and acid sampling, that the ports for sampling are placed at the entrance of the respective absorption vessels, so that the sample in question represents, in case of liquid, the concentration as it leaves the vessel, and, in case of the gas, the entering concentration.

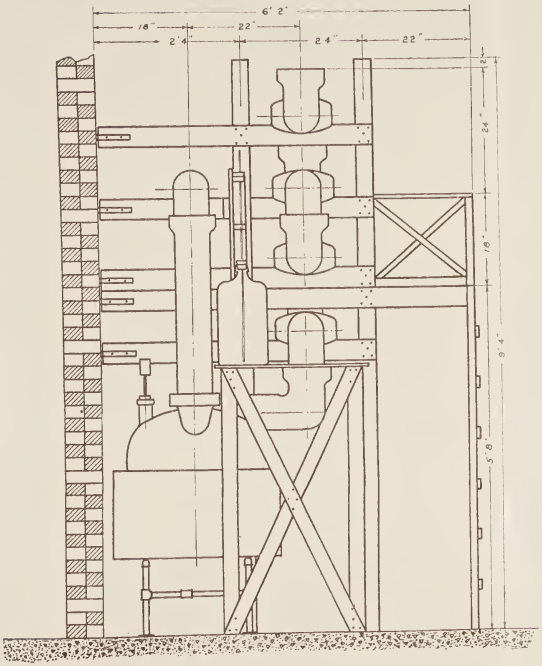
[1] *Chem. Met. Eng.*, 27, 223–5 (1922).

# VITREOSIL ABSORPTION SYSTEM

SCALE: $\frac{1}{2}$" = 1'-0"

J.R. Withrow
H.E. Fritz



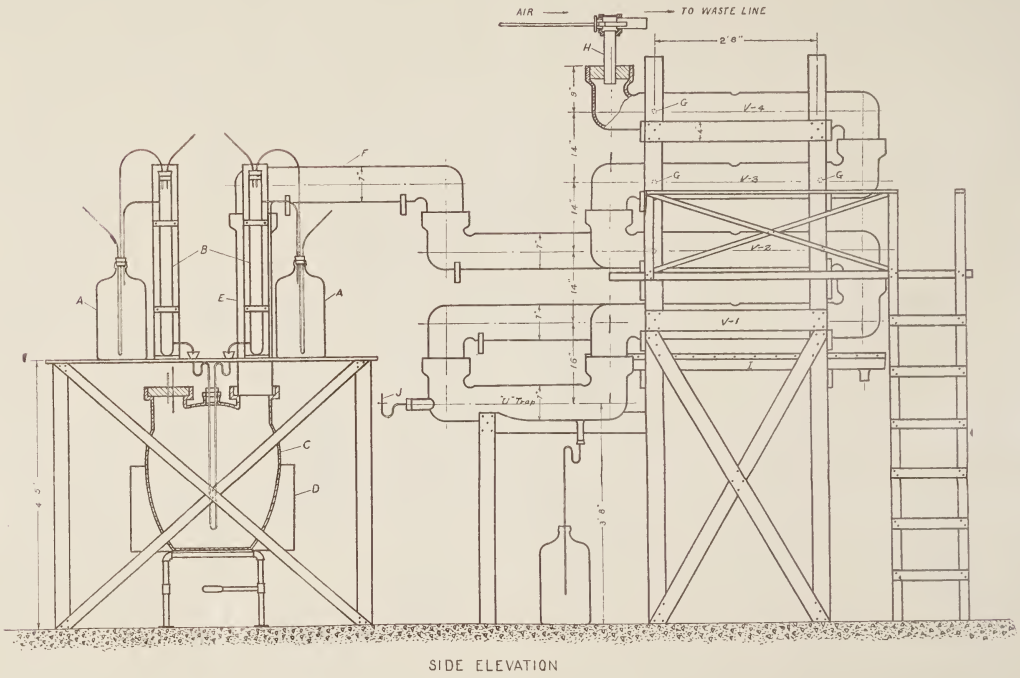




Fig. 1. Vitreosil Absorption System.

## Hydrochloric Acid Absorption Data Sheet for Vitreosil Absorption System

April 18, 1923.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | | | | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Date | Runs | Duration of Run | HCl Gas Conc. Desired | Generator | U Trap | Vessels | | | | Exit | Acid Make | Specific Gravity | Absorpt. Area Utilized | Acid Made per Sq. Ft. Hr. 1.175 Sp. Gr. at 20° C. | HCl Gas Absorbed per Sq. Ft. per Hour | HCl Gas Absorbed per Sq. Ft. per Hour Stan. Cond. |
| | No. | Hrs. | Gas % | Gas Conc. % | Gas Conc. | 1 | 2 | 3 | 4 | Gas Conc. % | Pounds per Run | At 20° C. | Sq. Ft. Vessels | In Pounds | In Pounds | In Cu. Ft. |
| 4–23... | 8 | 6 | 100 | 98 | 97 | 94 | 12 | 00 | 00 | 00 | 88 | 1.180 | 3.08 | 4.89 | 1.7071 | 16.729 |
| 10–23... | 4 | 6 | 75 | 70 | 68 | 65 | 20 or 30 | 00 | 00 | 00 | 110 | 1.152 | 3.52 or 3.97 | 4.37 or 4.08 | 1.5081 or 1.4243 | 14.779 or 13.958 |
| 12–23... | 5 | 6 | 50 | 50 | 47 | 45 | 22 | 00 | 00 | 00 | 89 | 1.175 | 4.66 | 3.18 | 1.1101 | 10.879 |
| 12–23... | 6 | 6 | 25 | 25 | 25 | 24 | 17 | 2 | 00 | 00 | 89 | 1.175 | 6.44 | 2.30 | 0.8029 | 7.868 |
| 14–23... | 6 | 6 | 10 | 13 | 13 | 13 | 9 | 3 | 00 | 00 | 90 | 1.175 | 7.47 | 2.00 | 0.6982 | 6.842 |

Average system pressure = Barometer, less 1/4 inch.

Average temperature of gases entering U trap = 25° C.
Average temperature of output acid = 37° C.
Average temperature of input feed water = 28° C.

Absorption area per vessel in square feet = 3.05.
Input cooling water = 10.5° C.
Output cooling water = 13.5° C.

J. R. Withrow,
H. E. Fritz.

Ohio State University,
Chemical Engineering

Each run was conducted over a period of six hours, sampling at the beginning of each hour. From these results the average for the total period was determined.

The effluent acid from each six-hour run was weighed, carefully mixed and the specific gravity of the mixture determined by means of a hydrometer. This hydrometer had been checked against titrations for acid content. The average output of acid per hour for each run was close to fifteen pounds of 1.175 sp. gr. acid at 20° C., or 21.6° Bé.

The gas concentrations were varied by injection of free air into the generator, thus serving the double purpose of agitating the mixture and diluting the acid vapor. In drawing up the final results the calculations were all based on the gas concentration as measured at the first vessel and 15 lbs. acid make per hour, sp. gr. 1.175 at 20° C.

The gas concentrations investigated were approximately one hundred, seventy-five, fifty, twenty-five, and ten per cent by volume, for the first portion of the work. These values serve to illustrate the behavior of the gases and equipment under general working conditions.

As the concentration of the acid vapor was diminished by injection of air, the initial velocity of gas travel through the equipment increased, thus introducing a variable for time of contact of acid vapors and absorbent. The collection of data on this item is as yet incomplete, but the velocities for each gas concentration are tabulated later in this paper. Variation in velocity during actual manufacturing plant operation can readily be imagined to be very large at times, though we know of no data on this subject. We purpose in our future work to eliminate this factor from our runs in one series at least. *The present work is based upon constant acid make.*

The averages of the data obtained (with respect to gas concentration) from each of five runs, using the gas concentrations mentioned above, are shown in the table.

## Derivation of Absorbing Area Requirements

In case of the last four columns (11), (12), (13) and (14), the information shown is the result of calculations as follows:

In column (11) marked "Absorbing Area Utilized," run number eight, the percentage gas in vessel number one is ninety-four, and in vessel number two it is twelve. If ninety-four per cent is the total

acid gas content entering vessel one, and twelve per cent is the total entering vessel two (or the equivalent of leaving vessel one), the part absorbed in vessel number one may be obtained as follows:

If ninety-four per cent of the total volume of gas entering vessel one is hydrochloric acid, the remaining six per cent is air, and this volume of air should practically remain constant throughout the system, though its percentage of the volume in subsequent vessels will materially increase. Hence, entering vessel number two, if the gas concentration is twelve per cent hydrochloric acid, the difference between this item and the total volume entering is equivalent to the air present in the mixture at this point, and this volume of air must be equivalent to the original amount of air entering vessel one. Therefore the six volumes per hundred of air entering the first vessel are equivalent to eighty-eight per cent of gas entering second vessel. Then by direct proportion twelve-eighty-eighths of six volumes is eight-tenths (0.8) volume of hydrochloric acid per hundred initial volumes of mixture which entered the first absorber and finally passes or escapes from the first absorber. Therefore if ninety-four volumes originally entered vessel one, it is evident that ninety-three and two-tenths (93.2) volumes were absorbed in the first vessel. This means that 93.2/94 of the total entering hydrochloric acid gas is absorbed in the first vessel.

In order to determine the portion of vessel two which is being utilized in this particular case, it would probably be reasonable to assume 93.2/94 equivalent to the total absorbing area of the first vessel (because all of number one is being utilized as indicated by acid gas leaving) and determine the equivalent of 0.8/94 (assuming that the available area of each vessel is the same) as representing the probable effective absorbing area required of the second vessel, though the figure is, of course, arbitrary.

$$\text{Therefore: } 93.2/94 = 3.05 \text{ sq. ft.}$$
$$1/94 = 0.032 \text{ sq. ft.}$$

If the figure is rounded off to be 1/94, then the total area utilized for ninety-four per cent gas under the conditions of the experiment would be $3.05 + 0.032 = 3.082$ sq. ft.

In case more than two vessels are being utilized, as in tabulated run number six, the method of calculation is as follows:

Twenty-four per cent is the gas concentration entering vessel one, seventeen per cent entering vessel two, and two per cent enter-

ing vessel three. Following the reasoning above, there would be seventy-six (76 vols.) per cent air entering the first vessel, and this quantity of air would remain constant at seventy-six volumes. Vessel two shows, eighty-three per cent air which would be equivalent to the seventy-six volumes entering vessel one; then

83 per cent = 76 vols.
17/83 = 15.56 vols. HCl entering vessel two.

In vessel three there is ninety-eight per cent air, therefore,

98 per cent = 76 vols. of air.
2/98 = 1.56 vols. HCl entering vessel three.

The difference in these two figures gives the volumes of HCl absorbed in vessel two.

15.56 − 1.56 = 14.00 vols. absorbed in vessel two.

Making the same assumption as above,

14/15.56 = 3.05 sq. ft.
1.56/15.56 = 0.339 sq. ft. of vessel three utilized.

All of vessels one and two were effective, and 0.339 sq. ft. of vessel three, the total effective area would then be the sum of all the areas: 3.05 + 3.05 + 0.339 = 6.439 sq. ft. total effective area.

In a similar manner all the items of column eleven have been derived.

The figure for the second vessel may at first seem to be in error, due to the lower gas concentration in each succeeding vessel, which really should require a larger absorbing area if all conditions were as in the first vessel. Actually the conditions are quite different in the second vessel and are to a certain extent compensatory in nature for while the gas concentration is lower it is also true that the absorbent in each succeeding vessel is more vigorous, due to lower acid concentration in the water flowing. The time of contact factor also is larger due to decreased volume of gas, as the result of prior absorption, and therefore materially lowered velocity. These opposing factors have been assumed to offset each other, and in the absence of more definite information, we have adopted these figures until further experiments yield correction factors.

It should be noted that under run four, two sets of figures are

given in each block; this is the result of two non-concordant runs, the average of both being given.

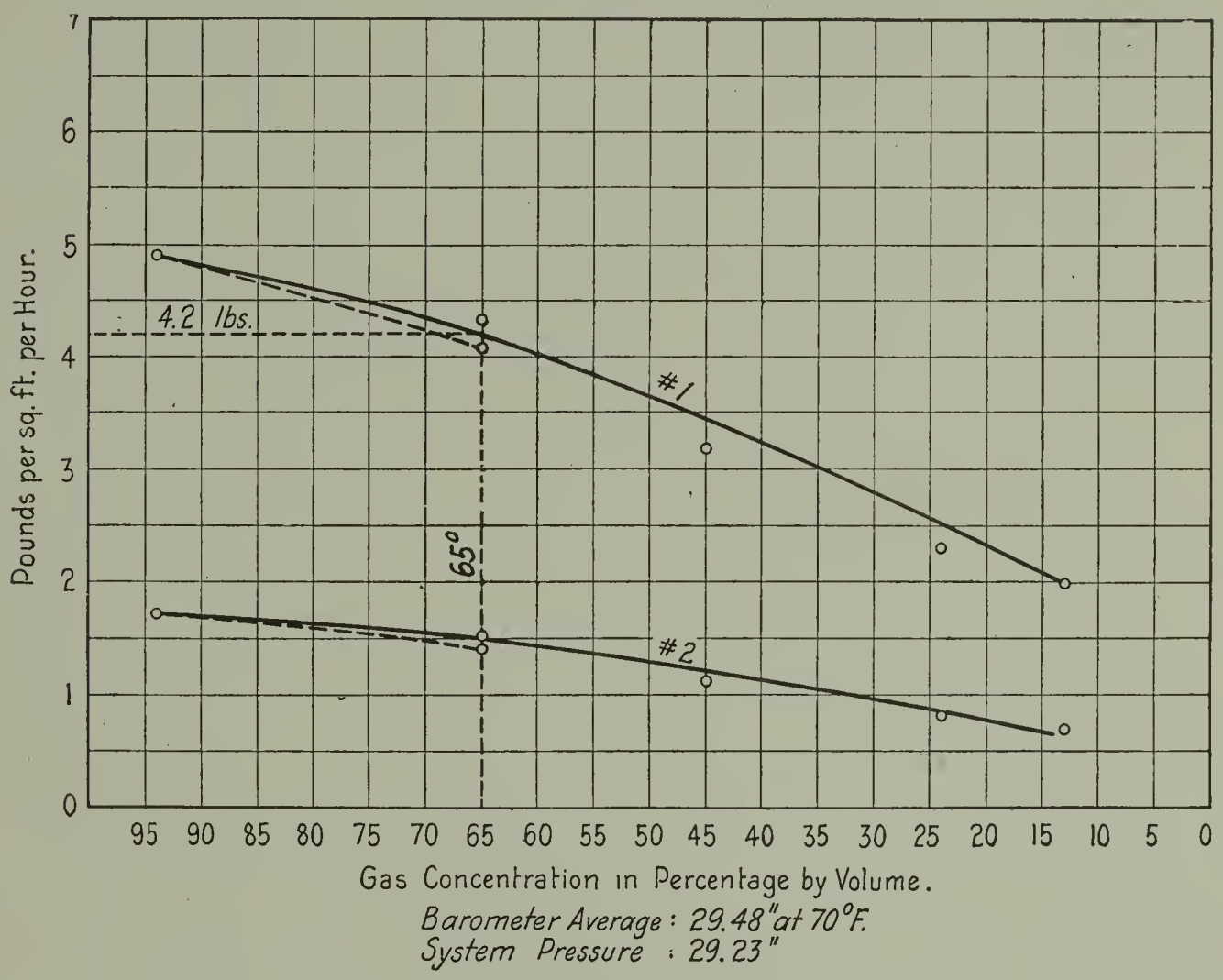



FIG. 2. Hydrochloric Acid Absorption.

Acid Make.

No. 1—Acid (Liquid) production.

No. 2—Gas (HCl) absorption.

Basis—1.175 sp. gr. at 20° C.

## GAS VELOCITIES AT FIRST ABSORBING VESSEL

### TABULATION OF INITIAL GAS MIXTURE VELOCITIES

Based on fifteen pounds of 1.175 sp. gr. (@ 20° C) acid per hour. Standard conditions.

| Lbs. HCl Gas (100%) per Hr. | Volume of 100% Gas. Cu. Ft. | Actual Gas Percentage First Vessel | Actual Gas Mixture Vol. (Calculated) | Velocity in Ft. Per Min. 760 mm. and 0° C. |
|---|---|---|---|---|
| 5.23 | 51.25 | 94.0 | 54.52 cu. ft. | 2.18 |
| 5.23 | 51.25 | 65.0 | 78.84 " " | 3.15 |
| 5.23 | 51.25 | 45.0 | 113.9 " " | 4.558 |
| 5.23 | 51.25 | 24.0 | 213.67 " " | 8.547 |
| 5.23 | 51.25 | 13.0 | 394.25 " " | 15.77 |

The table only refers to the initial velocity directly over the absorbent in the first vessel. Assuming that the gas mixture approximately obeys the gas laws, an expansion factor, for pressure and temperature changes of 1.136, will apply here, and by multiplying the velocity given under standard conditions by this figure, the velocity under experimental conditions will be obtained.

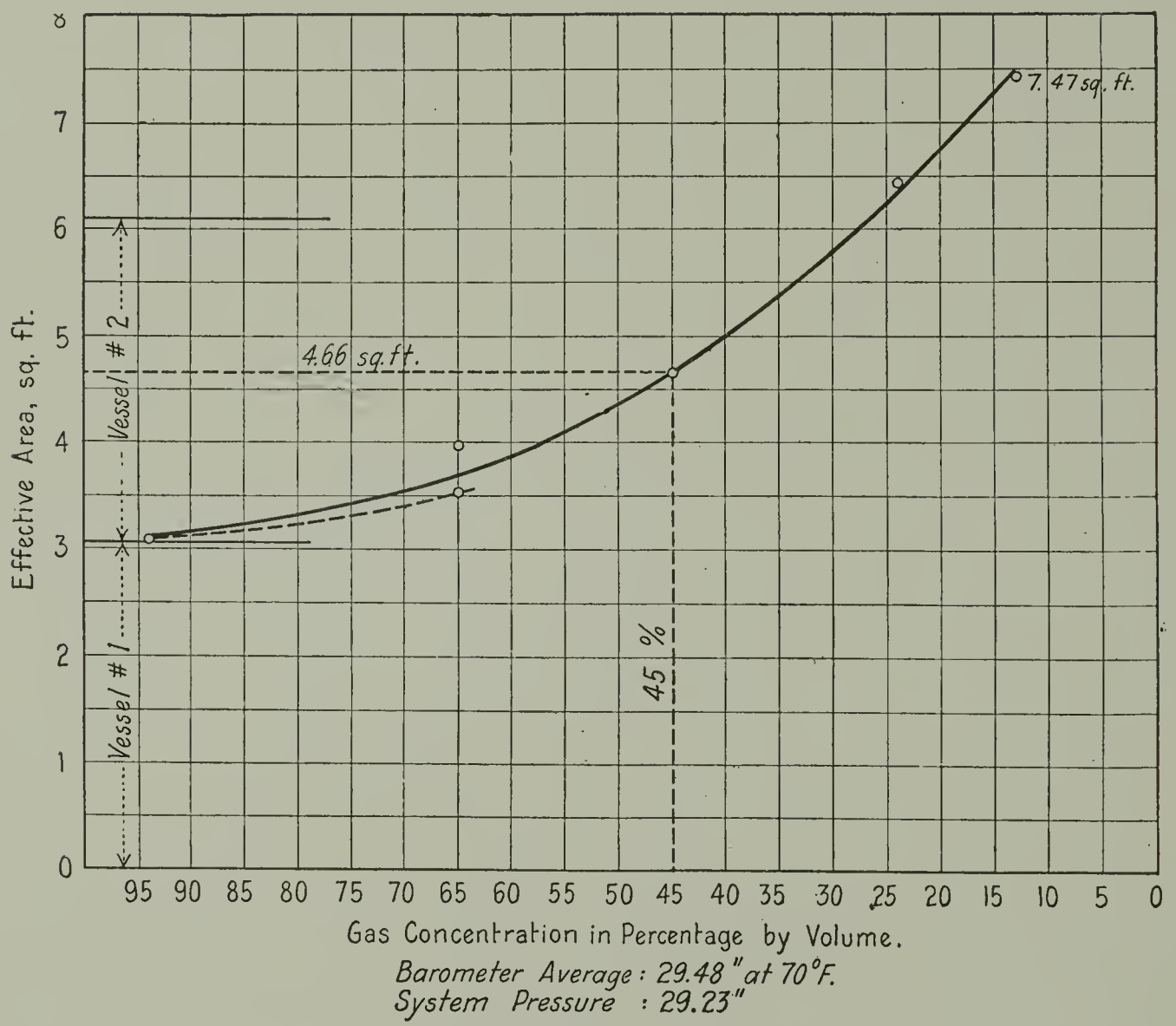



FIG. 3. Hydrochloric Acid Absorption.

Effective Area.
Basis 15 pounds acid per hour.
Sp. gr.—1.175 at 20° C.

*Graphs.*—From the tabulated data sheet, graphs have been prepared to represent the various derived results. These graphs are so marked as to be self-explanatory, except in the case of run four (65 per cent gas); in this case the heavy line represents the average of the two runs mentioned, the dotted lines the true path for each run.

## Conclusions

1. This investigation shows that small quantities of HCl can be completely absorbed in the Tyler Vitreosil system.

2. It is practical to get complete "scrub-up" with both high and low gas concentrations in this form of equipment even though the surface of contact is limited as compared with tower design.

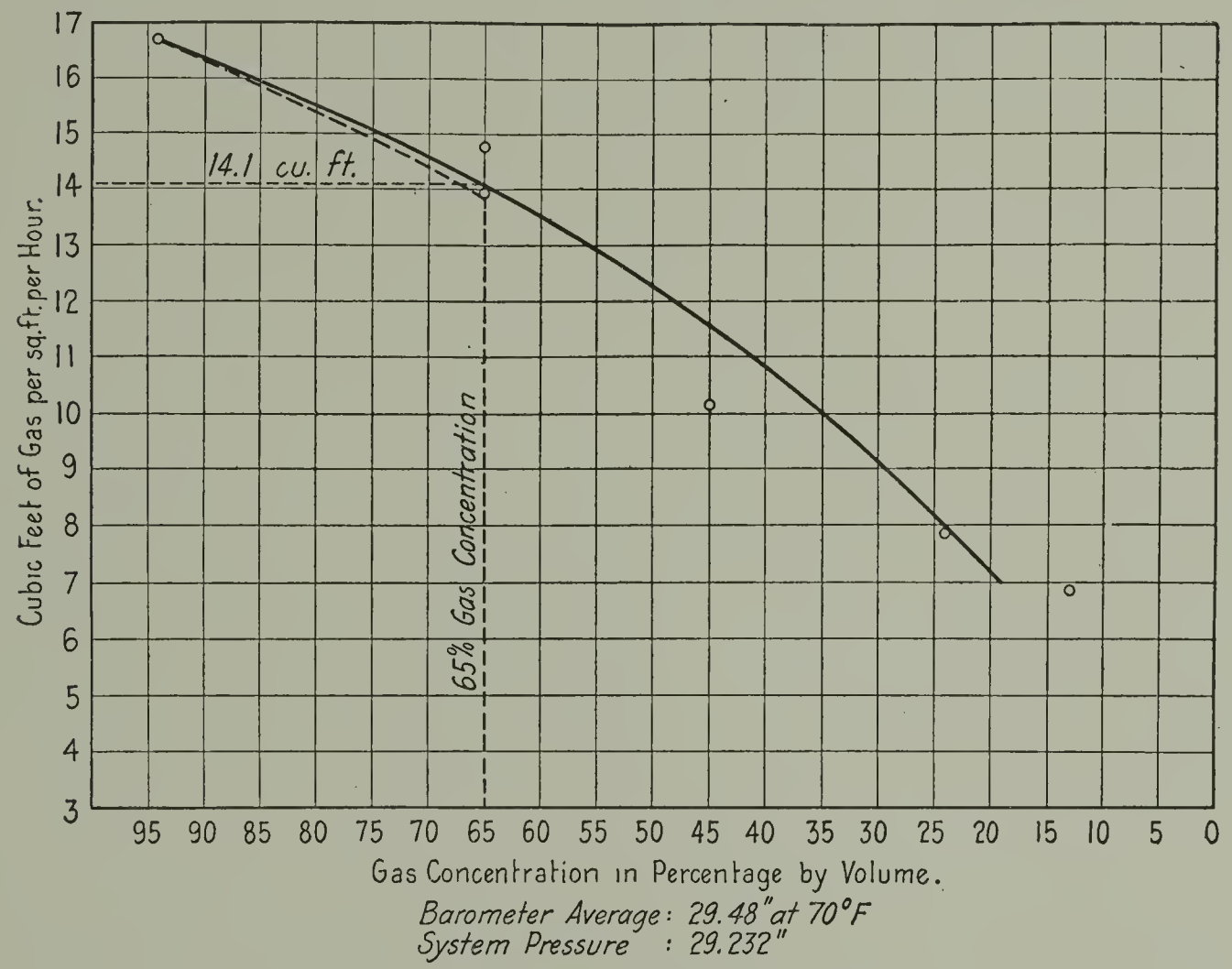



Fig. 4. Hydrochloric Acid Absorption.
Gas Absorbed.
Cubic Feet.
Basis * 1.175 sp. gr. at 20° C.

3. This work shows the marked difference in the absorbing power of this absorption equipment for differences in gas concentration. This is in line with the facts previously known qualitatively only, regarding any system but now given a quantitative value.

4. The method of calculating the effective area in case of the absorption vessel which is not being fully utilized, if in error to any appreciable extent would in our opinion be to the disparagement of the equipment. We have made our assumptions with this in mind

so that our figures would be conservative and prevent selection of insufficient absorption capacity in any given case.

5. The zone in which this work has been conducted, viz., high gas concentration, will apply to the manufacture and absorption of acid from three sources, namely: with the synthetic process in which the gas concentrations may go as high as fifty to sixty per cent and with the so-called "closed roaster" type of salt cake furnace, in which the gas may go as high as thirty-five per cent, and from chlorination of hydrocarbons in which the gas concentration may go as high as 90–98%.

6. The results do not apply to "open roasters" or mechanical furnaces in which the gas concentration may go as low as one and one-half per cent. They of course do not apply even in the cases mentioned in conclusion two, when air access or other factors lower the acid gas concentration below fourteen per cent, nor do they apply to maximum velocity operation.

*Note.*—The writers are indebted to Mr. D. M. Phillippi, of this laboratory, for faithful assistance in this work, and to Messrs. Winship and Tyler, of the Thermal Syndicate, Ltd., for cooperation on the equipment.

LABORATORY OF INDUSTRIAL CHEMISTRY,
THE OHIO STATE UNIVERSITY,
April, 20, 1923

## DISCUSSION

DR. WILLIAMS: May I ask Professor Withrow whether he has tried the same scrubbing device for gases other then hydrochloric acid, for instance, ammonia gases, with similar results?

DR. WITHROW: We have only had this setup for two months, and there is an immense amount of work ahead to be done on hydrochloric acid gas. We need data on this, as I understand there are large units to be erected in this country with maximum capacity. No other gas has been tried except hydrochloric acid. (Communicated) an iron system would of course serve for ammonia.

PRESIDENT HOWARD: I think this investigation is very interesting, and will be a very helpful one to chemical engineers who have to design apparatus for condensation of hydrochloric acid.

DR. BARR: Is there any small tower in the bend?

DR. WITHROW: No. It has been suggested that with lower gas concentrations it may be necessary to have towers. Mr.

Tyler is here, I believe, and I wish he would discuss that question. In his original paper he showed that towers may be inserted, but we have not used them. We simply investigated the rate of absorption in the S-bend connections themselves.

MR. STEPHEN L. TYLER: I should like to state that in Dr. Withrow's figures, as you have probably noted, the maximum absorption of hydrochloric acid gas is 1.7 pounds per square foot per hour. Unfortunately I do not have figures available to give results on complete operations in commercial units, although absorptions have been obtained in test units working on commercial gases of as high as seven pounds per square foot per hour with low concentration acid gas.

In connection with the use of intermediate towers no installation has been made as yet using these. These towers were included in the original designs as shown in conjunction with my paper presented a year ago. The object of these towers is to allow of a complete scrub-up of the gases thus eliminating the use of the final scrubbing tower. With this type of construction it would be possible to use a tower packing which would be highly acid-proof and which would not introduce any impurities into the acid.

It is hoped that in the near future we will have complete figures on the absorption vessel operating with the bare absorption vessel also the absorption vessel used in conjunction with intermediate towers.

PRESIDENT HOWARD: If there is no further discussion we will proceed to the next paper.

# CALCULATION OF VAPOR RECOMPRESSION EVAPORATORS

Read at Wilmington, Del., Meeting, June 22, 1923.

By L. A. PRIDGEON

The essential organs of a vapor recompression evaporator are shown in Fig. 1. They are a preheater for heating the feed liquor with the condensate leaving the evaporator, an evaporator, and a compressor, which in this case is a motor-driven turbo-blower.

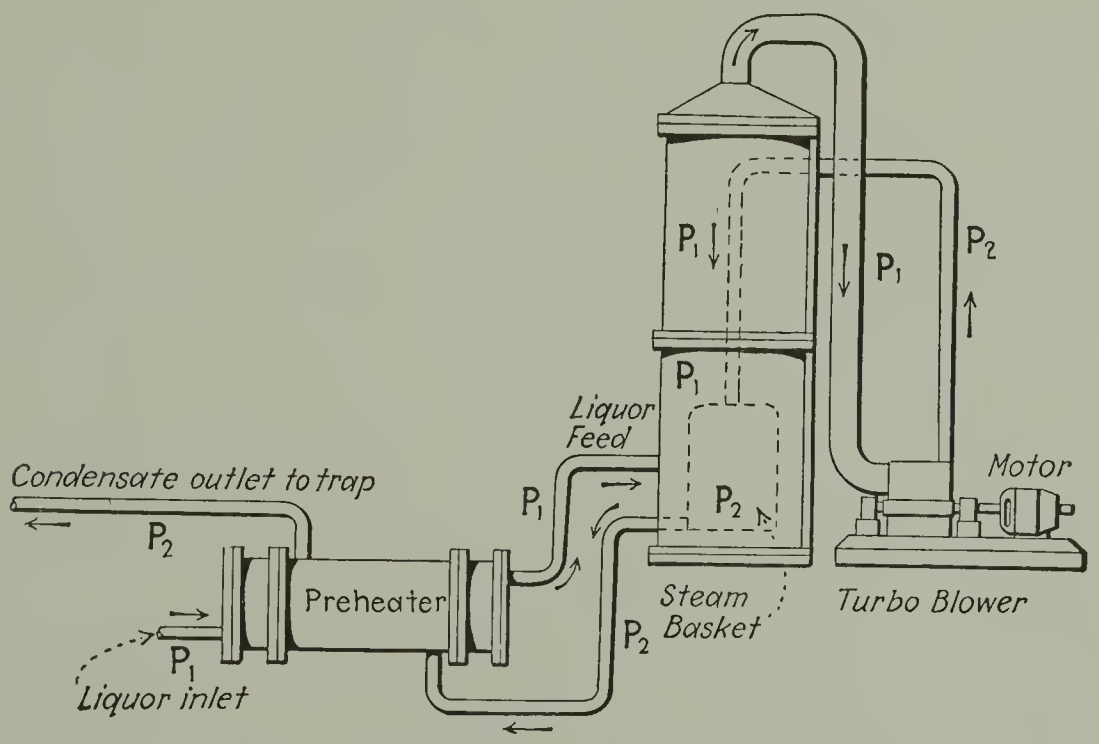



FIG. 1. Vapor Recompression Evaporator

It should be noted that there are two parts to the fluid circuit, the high pressure, $P_2$, and the low pressure, $P_1$; also that any portion of the fluid traverses the circuit but once. The fluid enters the low-pressure circuit at the preheater as feed liquor, passes through the preheater into the body of the evaporator, vaporizes and leaves through the vapor line to the compressor. The fluid enters the high-pressure circuit at the discharge side of the compressor, passes to the steam basket, condenses, leaves the machine through the preheater, and is collected in a trap below the evaporator.

The action of the machine may be studied to advantage in connection with the temperature-entropy diagram shown in Fig. 2.

The vapor is drawn into the compressor through the suction pipe from the vapor space of the evaporator. It may be assumed that the vapor entering the compressor is in the saturated state at the temperature $T_1$, which may be taken equal to the temperature corresponding to the pressure $P_1$ in the vapor space of the evaporator. This state is represented by point $B$. The vapor is compressed adiabatically to a final pressure $P_2$, which is the pressure corresponding to the temperature $T_2$ of saturated steam in the steam basket. Adiabatic compression is represented by $BC$.

The superheated vapor in the state $C$ is discharged into the steam basket, where heat is abstracted from it by the liquor in the evaporator. First the superheated vapor is cooled to the state of saturation; this process is represented by the line $CD$, and the heat abstracted by the area $C_1CDD_1$. Then heat is further removed at the constant temperature $T_2$ (and pressure $P_2$) and the vapor condenses. At the end of the process the fluid is in the liquid state. Its state is represented by the point $E$ on the liquid curve, and the heat abstracted by the area $D_1DEE_1$. The condensate then leaves the steam basket and enters the preheater, where it is cooled to the temperature $T_3$ of the entering liquor. Its state is represented by the point $F$ and the heat abstracted by the area $E_1EFF_1$.

The feed liquor enters the preheater at the temperature $T_3$, and its state is represented by the point $F$. In this theoretical case the temperature of the condensate leaving the preheater is taken as the temperature of the entering feed liquor. The reason for this is obvious from the discussion that follows. In practice, however, the temperature of the condensate leaving the preheater would be above that of the entering feed liquor. The temperature of the liquor entering the evaporator lies along the line $FA$. Assuming no elevation of boiling point, the liquor is raised to the temperature $T_1$, corresponding to the pressure $P_1$ of the vapor space. Its state is then represented by the point $A$, and the heat absorbed in raising its temperature from $T_3$ to $T_1$ is represented by the area $F_1FAA_1$. The temperature of the vapor in the steam basket being higher than that of the liquor, heat is absorbed by the liquor and it vaporizes at constant pressure $P_1$. This process is represented by the line $AB$ and the heat absorbed from the vapor in the steam basket by the area $A_1ABC_1$.

The work done on the fluid is the difference between $Q_1$, the

heat absorbed by the liquor, and $Q_2$, the heat rejected to the steam basket and preheater. We have then

$$Q_2 = \text{area } C_1CDEFF_1$$
$$Q_1 = \text{area } F_1FABC_1$$

The area $F_1FAA_1$ is common to both.

Therefore, if $AW$ represents work expressed as heat units,

$$AW = \text{area } C_1CDEAA_1 - \text{area } A_1ABC_1$$
$$= \text{area } BCDEAB$$

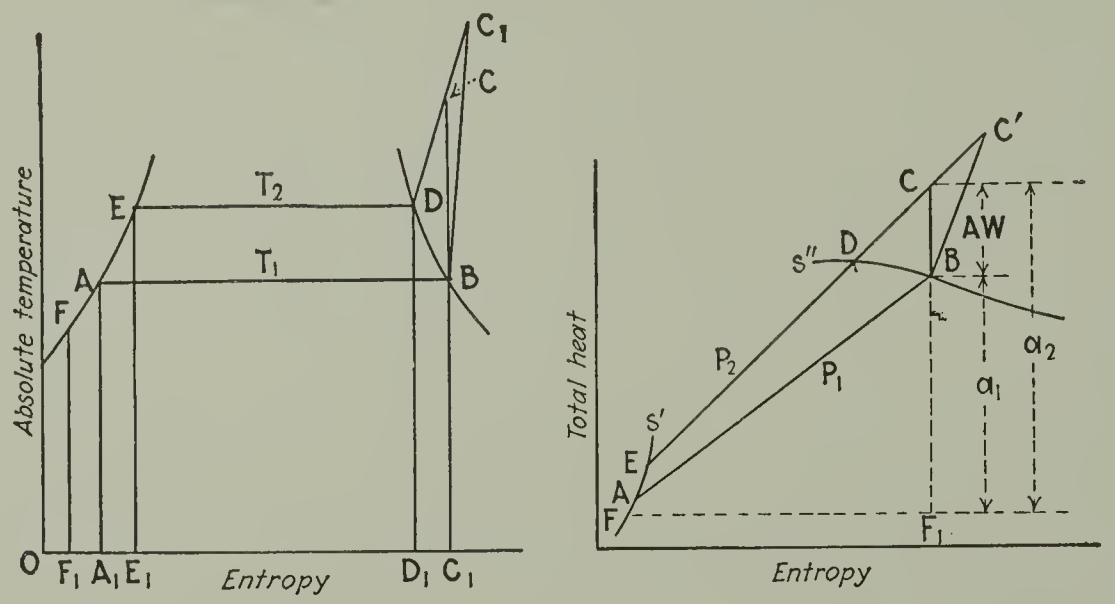
In the cycle above described, the heat rejected to the steam basket and preheater is equal to the heat absorbed by the liquor, therefore $Q_2 = Q_1$ and $AW = 0$. In practice, a temperature difference must be maintained between the heating steam and the exaporating liquor, and a temperature difference consequently implies a pressure difference. Therefore $AW$ cannot be equal to zero. Since work is done in maintaining this pressure difference, means must be provided for removing this work from the system in the form of heat. In this particular case this can be done in only two ways: heat removed by the thick liquor and by radiation. These being constant, $AW$ is constant and therefore the temperature difference is constant and rather small.

The amount of heat added to any system in a given time must necessarily be taken away from the system in the same time if the initial condition of the system is to be maintained. So in our case if a specified temperature difference (which is a pressure difference) is to be maintained between the steam and boiling liquor by the compressor, the heat added by the compressor in the form of work must be removed. If the heat lost by radiation and through thick liquor discharge is not sufficient to remove all the heat added by compression, it will be necessary to blow off steam from the vapor space. If steam were not blown off, the pressure of the vapor space would rise and thus decrease our temperature difference, thereby decreasing the work of compression and decreasing the heat added to the system in unit time. If the heat discharged from the system by radiation and through thick liquor is greater than that added by work of compression, heat must be added from some external source in order to maintain the specified temperature difference. If heat is not added from an external source, the temperature difference will increase until the work of compression is equal to the heat lost

from the system by radiation and through thick liquor. With a given set of conditions it is impossible to maintain a predetermined temperature difference. The machine will come to equilibrium and maintain its own temperature difference. If no heat were lost from the apparatus, the boiling point would rise to that of the steam temperature, and there would be no temperature difference and consequently no evaporation. The temperature difference is a function of the net amount of heat lost from the apparatus per unit time.

## Calculation of Work Required

The cycle of the vapor recompression evaporator transferred to the total heat-entropy plane is shown in Fig. 3. (This figure is a part of the Mollier diagram, which can be found in Marks and Davis' "Steam Tables and Diagrams.") The same letters in Figs. 2




Figs. 2 and 3. Temperature-entropy and Heat-entropy Diagrams

and 3 denote the same states. Adiabatic compression is represented by $BC$, the point $B$ lying on the saturation curve $S''$ (dry and saturated steam) at its intersection with the constant pressure line $P_1$. Line $CE$ represents the cooling and condensation of the steam at constant pressure $P_2$, and line $EF$ the cooling of the condensate in the preheater. The heat $q_2$ given up by unit weight of steam in the steam basket and by the condensate in the preheater is therefore the difference of thermal potential (total heat) between the states $C$ and $F$:

$$q_2 = ic - if \ (i = \text{total heat in 1 lb. of steam})$$

This heat is represented by the segment $CF_1$. Point $E$ represents condensate at the pressure $P_2$ in the steam basket. Point $A$ repre-

sents the state of the condensate leaving the preheater and the state of the liquor entering the preheater. The process $FA$ is the heating of the liquor in the preheater, and the process $AB$ is the vaporization in the evaporator, during which heat $q_1$ is abstracted from the preheater and steam basket.

$$q_1 = ib - if$$

This heat is represented by the segment $BF_1$

$$AW = q_2 - q_1 = (ic - if) - (ib - if) = ic - ib$$

That is, the work required in thermal units is the change of thermal potential during the adiabatic compression.

If $M$ equals the weight of liquid evaporated per hour, the work required per hour expressed in thermal units is $M\ (ic - ib)$, and the net power in kilowatts required to drive the machines equals

$$M\frac{(ic - ib)}{3420}$$

If $n$ = efficiency of the compressor

$$\text{Gross kw.} = M\frac{(ic - ib)}{3420n}$$

The conceptions of steam compression differ from air compression in that adiabatic instead of isothermal compression is taken as 100 per cent efficiency. Steam compressors are not 100 per cent efficient. Internal friction between the moving parts and between the steam and its path through the compressor is converted into heat, which tends further to superheat the compressed vapor above that corresponding to adiabatic compression. This causes an increase in total heat, entropy and temperature without increasing the pressure.

If the compressor were water-jacketed this superheat could be removed at least in part. The work of compression for a given pressure difference would be decreased, thus increasing the efficiency of the compressor. The heat taken up by the water jacket is not available for evaporation, as it would be if allowed to remain as superheat in the compressed steam. Waterjacketing compressors is established practice in air compression. It might well be con-

sidered in connection with steam compression. In the following problems, however, the compressor is assumed to be not water-jacketed. Since the compressor is not 100 per cent efficient, compression is represented in Fig. 2 and Fig. 3 by the line $BC'$ and not by $BC$.

Following are four problems representing hypothetical cases and are not to be taken as the conditions that actually exist but conditions that are assumed to exist.

### Problem I

How much power is required to evaporate 10,000 lb. water per hour from a solution boiling at 212 deg. F., assuming heat losses by radiation, etc., are equal to the heat added in form of work to maintain the temperature difference of 18 deg. F.? Compressor and motor efficiency 60 per cent (based on adiabatic compression as 100 per cent).

*Solution*—A temperature of 230 deg. F. corresponds to a pressure of 20.77 lb. for dry and saturated steam. To find the total heat in a pound of steam which has been compressed adiabatically from 14.7 lb. to 20.77 lb., start on the Mollier (total heat-entropy) diagram at the intersection of the constant pressure line 14.7 lb. with the saturation curve and follow the constant entropy line vertically upward to the constant pressure line 20.77 lb. and read at the left of the diagram off the constant total heat line 1,177 B.t.u.

The power required is:

$$\frac{M(ic - ib)}{3420n} = \frac{10{,}000(1177.0 - 1150.4)}{3420 \times 0.60} = 129.5 \text{ kw.}$$

### Problem II

From 12,000 lb. of solution fed to the evaporator per hour 10,000 lb. is evaporated. Boiling point is 212 deg. F., vapor dry and saturated. Liquor enters preheater at 60 deg. F. Condensed steam leaves preheater at 100 deg. F. Radiation 0.25 per cent (based on evaporation). Compressor efficiency 63 per cent (based on adiabatic compression as 100 per cent). Motor efficiency 95 per cent. Specific heat of solution leaving and entering is 1.

(*a*) What is the temperature difference?

(*b*) How much power is required?

(*c*) If the coefficient of heat transmission is 250 B.t.u. per hr. per deg. F. per sq. ft., how much heating surface is required in the evaporator?

*Solution*—To simplify calculations, use 60 deg. F. as a datum for calculating total heat entering and leaving machine.

*Heat entering apparatus:*

(*a*) Heat entering the apparatus as such equals 0, as the feed liquor enters at 60 deg. F.

*Heat leaving apparatus:*

(*a*) In condensate

$$10{,}000(100 - 60) = 400{,}000 \text{ B.t.u.}$$

(*b*) In thick liquor

$$2{,}000(212 - 60) = 304{,}000 \text{ B.t.u.}$$

(*c*) By radiation

$$10{,}000 \times 970.4 \times 0.0025 = 24{,}260 \text{ B.t.u.}$$

Total 728,260 B.t.u.

All of this 728,260 B.t.u. leaving the apparatus is added by the compressor in the form of work; therefore

$$\frac{728{,}260}{10{,}000} = 72.8 \text{ B.t.u. added to each pound of vapor by the compressor.}$$

1150.4 + 72.8 = 1223.2 B.t.u. total heat in 1 lb. of heating steam. If the compressor were 100 per cent efficient, use the figure 1223.2. Since the compressor is 63 per cent efficient use 1150.4 + (72.8 × 0.63) = 1196.2. To find the pressure of the steam leaving the compressor enter the Mollier diagram at 1196.2 and move horizontally to right to a point on constant entropy line directly above the intersection of the saturation curve with the constant pressure line for 14.7 lb. This falls on the constant pressure line for 26.4 lb. The temperature corresponding to 26.4 lb. from steam tables is 243.1 deg. F. The temperature difference is 243.1 − 212 = 31.1 deg. F. Temperature differences are taken as the difference in temperature between dry and saturated steam at the pressure $P_2$ and the temperature of the boiling liquid. From steam tables steam at 26.4 lb. with a total heat of 1,223.2 B.t.u. is superheated 130 deg. F. The actual temperature of the steam is 243.1 + 130 = 373.1 deg. F.

(*b*) The power required is:

$$\frac{M(ic - ib)}{3420n} = \frac{10{,}000 \times (1196.2 - 1150.4)}{3420 \times 0.63 \times 0.95} = 229 \text{ kw.}$$

(*c*) The heating surface $= \dfrac{10{,}000 \times 1011.6}{250 \times 31.1} = 1300$ sq. ft.

## Problem III

Conditions are the same as Problem II except vapor is wet. The quality is 99.

(*a*) From the Mollier diagram the total heat in a pound of vapor at 14.7 lb. and quality 99 is 1140.4. The total heat in 1 lb. of heating steam is 1140.7 + 72.8 = 1213.5 B.t.u.

If the compressor were 100 per cent efficient, use the figure 1213.5. Since the compressor is 63 per cent efficient, use 1,140.7 + (72.8 × 0.63) = 1,186.5. To find the pressure of the steam leaving the compressor, enter the Mollier diagram at 1,186.5 and move horizontally to the right to a point on the constant entropy line directly above the intersection of the constant quality 99 with the constant pressure line for 14.7 lb. This falls on the constant pressure line 26.8 lb. The temperature corresponding to 26.8 lb. from the steam tables is 244 deg. F. The temperature difference is 244 − 212 = 32 deg. F. From the steam tables steam

at 26.8 lb. with a total heat of 1,213.5 B.t.u. is superheated 107 deg. F. The actual temperature of the steam is 244 + 107 = 351 deg.F.

(*b*) The power is the same as in Problem II.

(*c*) The heating surface $= \frac{10{,}000 \times 1001.1}{250 \times 32} = 1250$ sq. ft.

## Problem IV

From 14,000 lb. of brine fed to an evaporator per hour 10,000 lb. of water is evaporated and 4,000 lb. of wet salt is drawn from the machine. Pressure in the vapor space is atmospheric. Elevation of boiling point is 15 deg. F., hence boiling point is 227 deg. F. Brine enters preheater at 60 deg. F. Condensed steam leaves preheater at 100 deg. F. Radiation 0.25 per cent (based on evaporation). Compressor efficiency 63 per cent. Motor efficiency 95 per cent. Specific heat of condensate taken as 1. Specific heat of wet salt taken as 0.30.

(*a*) What is the temperature difference?

(*b*) How much power is required?

(*c*) If the coefficient of heat transmission is 250, how much heating surface is required in the evaporator?

*Solution*—As in Problem II, use 60 deg. F. as a datum.

*Heat entering apparatus:*

(*a*) Heat entering apparatus as such equals 0, as brine enters at 60 deg. F.

*Heat leaving apparatus:*

(*a*) In condensate

$$10{,}000(100 - 60) = 400{,}000 \text{ B.t.u.}$$

(*b*) In wet salt

$$4{,}000 \times 0.3(227 - 60) = 200{,}400 \text{ B.t.u.}$$

(*c*) By radiation

$$10{,}000 \times 970.4 \times 0.0025 = 24{,}260 \text{ B.t.u.}$$

Total 624,660 B.t.u.

624,660 = 62.5 B.t.u. added to each pound of vapor by the compressor. 1150.4 + 62.5 = 1212.9 total heat in 1 lb. of heating steam. If the compressor were 100 per cent efficient, use the figure 1212.9. Since the compressor is 63 per cent efficient, use 1150.4 + (62.5 × 0.62) = 1189.8. Using the Mollier diagram as before, find the pressure of the steam leaving the compressor to be 24.4 lb. The temperature corresponding to 24.4 lb. is 238.7 deg. F. The temperature difference is 238.7 − 227.0 = 11.7 deg. F. From the steam tables, steam at 24.4 lb. with a total heat of 1212.9 B.t.u. is superheated 111 deg. F. The actual temperature of the steam is 238.7 + 111 = 349.7 deg. F.

(*b*) The power required is:

$$\frac{10{,}000 \times (1189.8 - 1150.4)}{3420 \times 0.63 \times 0.95} = 192.4 \text{ kw.}$$

(*c*) The heating surface is:

$$\frac{10{,}000 \times 1005.9}{250 \times 11.7} = 3340 \text{ sq. ft.}$$

Department of Chemical Engineering,
University of Michigan

## Discussion

Professor W. L. Badger: I wish to point out one thing in Mr. Pridgeon's paper which, so far as I know, has never been mentioned in previous literature on the subject: that is, the relation between the losses from the evaporator and the temperature drop at which it works.

In ordinary calculations a certain working temperature drop is assumed and then capacity and steam economy are calculated on this bases. Apparently it has never been recognized that this working temperature drop is not a thing which we can regulate, but is something which the evaporator determines for itself, in order to maintain its own thermal equilibrium.

If we wish to emphasize steam economy we base our calculations on a small temperature drop and therefore sacrifice capacity; or in other words, make a very large evaporator necessary. We may, on the other hand, sacrifice steam economy, designing on the basis of a larger temperature drop and getting a more reasonable capacity. The question of whether or not the evaporator operates with the temperature drop we have assumed is answered by the balance of heat lost against power input; and not at all by our design. If we wish a small working temperature drop, we must keept the heat losses small or add steam from an external source. If we wish a larger temperature drop, we must increase the heat losses; or we may even have to blow off steam from the evaporator.

The cost of operation in an evaporator using vapor recompression is, of course, made up of two major items; (1) cost of equipment, and (2) the cost of steam for operation. If the temperature drop is made too small the cost of steam will be very small; but, because of low capacity, the evaporator will have to be very large; and therefore the first cost will be large. If the working temperature drop is very large, the first cost will be small, but the steam or power consumption will be excessive. The optimum operating conditions will be at some intermediate point, and the designer can not effectively fix this in advance. With an evaporator actually in operation, the temperature drop (and therefore the cost of evaporation) may be altered at will, by slightly altering the losses. This last may be done in a number of ways; such as changing the temperature of the feed, changing the amount of heat insulation, changing the temperature or quantity of thick liquid removed, or, finally,

adding steam from an external source in one case, or blowing off steam from the evaporator in the other case.

We are probably ahead of the times in discussing vapor recompression evaporators in detail. I do not know of any recompression evaporator operating in the United States. There is, however, a definite field for this equipment; and sooner or later we shall see numbers of them in the operating conditions where they are indicated.

# THE REFINING AND RECOVERY OF PETROLEUM PRODUCTS WITH SILICA GEL

By ERNEST B. MILLER

Read at the Wilmington, Del., Meeting, June 20, 1923

## Introduction

In the summer of 1918 intensive experimental work was begun at the laboratories of The Davison Chemical Company, Baltimore, Md., to develop the uses of silica gel for a number of industrial applications, which at that time seemed the most promising. After several months of work it became apparent that there were few basic industires to which silica gel did not have a more or less vital application, and our most difficult problem was to avoid scattering our energies over too many problems and thereby indefinitely postponing the perfecting of any one to a commercial success.

I shall not attempt, therefore, to discuss all manufacturing processes to which we may in the future be able successfully to apply silica gel, but shall confine myself to the economic aspect of its application to one of our most important industries, viz: the refining and recovery of petroleum products.

## Properties of Silica Gel

Silica gel is by this time known to a great many technical men, but a brief description of its structure and some of its characteristics due to this structure, may be welcomed by those not already familiar with the same.

The word "gel" does not accurately suggest the physical nature of the material as used, but rather refers to its condition at one stage of its manufacture. As actually used, it is a hard, glassy material, with the appearance of a clear quartz sand, and of the chemical formula $SiO_2$. The thing that differentiates this unique material from ordinary sand, however, is its highly porous structure, and especially the size and uniform arrangement of these pores.

It is made by mixing, in proper proportions and in a pre-determined manner, solutions of sodium silicate and sulphuric acid. After several hours this mixture sets to a homogeneous jelly-like

mass, which is called hydrogel. This hydrogel is then broken into pieces about one inch in size, and thoroughly washed to free it of sodium sulphate and excess acid. It is subsequently dried in a carefully regulated manner until it has shrunk to constant volume (about 10 per cent of its original volume), and is then known as silica gel, and ready for the final activation necessary before being used in any of its many applications. Before this final activation, silica gel may contain as much as 41 per cent of its own weight of water, even though it has been dried down to minimum volume and is to all appearances quite dry.

In this condition, the ultramicroscopic pores, which form approximately 41 per cent of its total volume, are virtually filled with water, and must be evacuated by further heating before these pores are available for the adsorption of liquefiable gases, or for other selective adsorption phenomena, notably the separation of solutes from non-aqueous solutions.

It is, of course, very difficult to describe the exact appearance of the internal structure of silica gel as it would appear if a microscope could be constructed of sufficient magnifying power to make it visible to the eye. But from our observation of its behavior under specified conditions, it would seem to consist of a uniformly arranged aggregation of extremely small spherical particles of pure $SiO_2$, such spherical particles touching one another and thereby forming voids between them which we have above referred to as pores of ultramicroscopic size. The surface of these particles in a given weight of silica gel is of truly startling dimensions. For instance, it can be mathematically determined that one gram of silica gel exposes an internal surface of approximately five thousand square feet. To this great surface in the first instance, in conjunction with the capillary action of the pores associated therewith, may be attributed all of the interesting characteristics exhibited by this material.

It is most fortunate that a material so chemically inert and able to withstand such high temperatures is capable of being put into the structural condition above described, since it can, therefore, be used almost universally without damage either to itself or to the products with which it may come in contact.

The question naturally asked is, what life does silica gel have when used over and over in practical industrial processes? The final answer to this question cannot be given as yet, since there

appears to be no actual deterioration in efficiency with repeated use, and the life of the material in constant use will be determined by the completeness with which physical losses of the silica gel can be avoided. The type of apparatus developed in which to use silica gel is such as to reduce physical losses of the gel to a minimum, but since the latter is nearly always used in pulverized form, and is circulated continuously, and mixed with the gases or liquids from which it is designed to adsorb certain constituents, an absolutely perfect recovery of all the gel entering the system is, of course, impossible. The loss is, however, too small to constitute a burdensome item of expense, nor will it be in any way a source of inconvenience to the process in which it is being used.

## Description of Apparatus

During the past four years we have designed, constructed in our own shops, and thoroughly tested a great variety of apparatus in which commercially to use silica gel. It was our aim to perfect one type of equipment that could be universally applied to all gas adsorption problems, and a second type to handle all applications to liquid purification. Except in special cases, where extremely high pressures must be maintained during the treatment of gases, the continuous type of adsorber using pulverized gel as illustrated diagrammatically in Plate No. 1, has proved applicable to every industrial problem that has to date come to our notice.

Likewise in the case of the treatment of liquids, we are able to use a combination of standardized equipment to accomplish the refining of any non aqueous liquid.

In some cases, as with lubricating oils and waxes, it is necessary to provide means for heating to a moderate temperature; but this has readily been accomplished without any change in the general character or arrangement of the integral parts of the plant. Such a plant is shown diagrammatically in Plate No. 4. We shall attempt only a general description of these two types of equipment, since the reader can no doubt follow the path of the gel through the cycle of operations, as well as the substance that is being treated.

## Gas Adsorption Plant

The silica gel is pulverized to about 200 mesh for use in this plant, and is brought in contact with the gas mixture by means

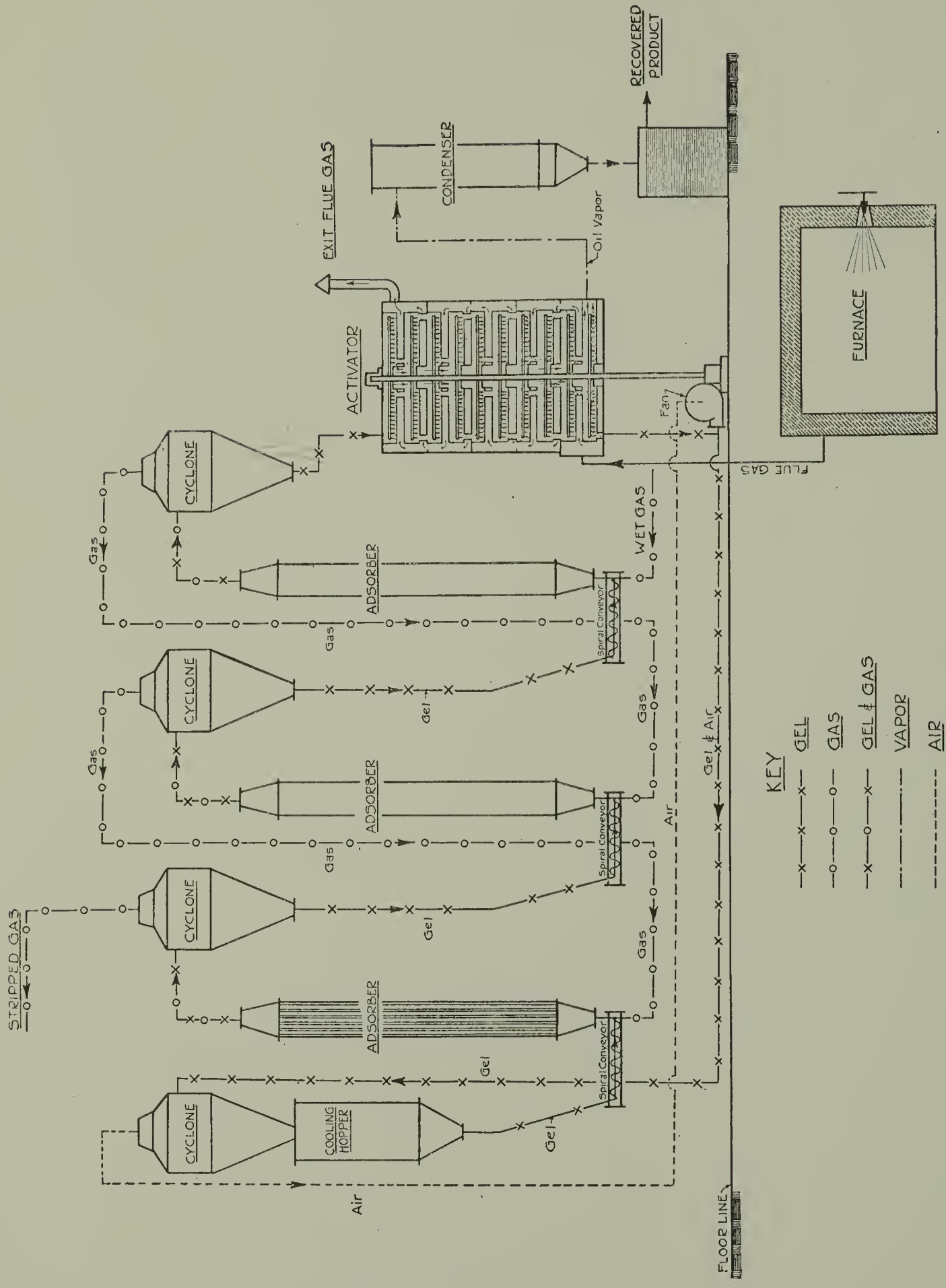
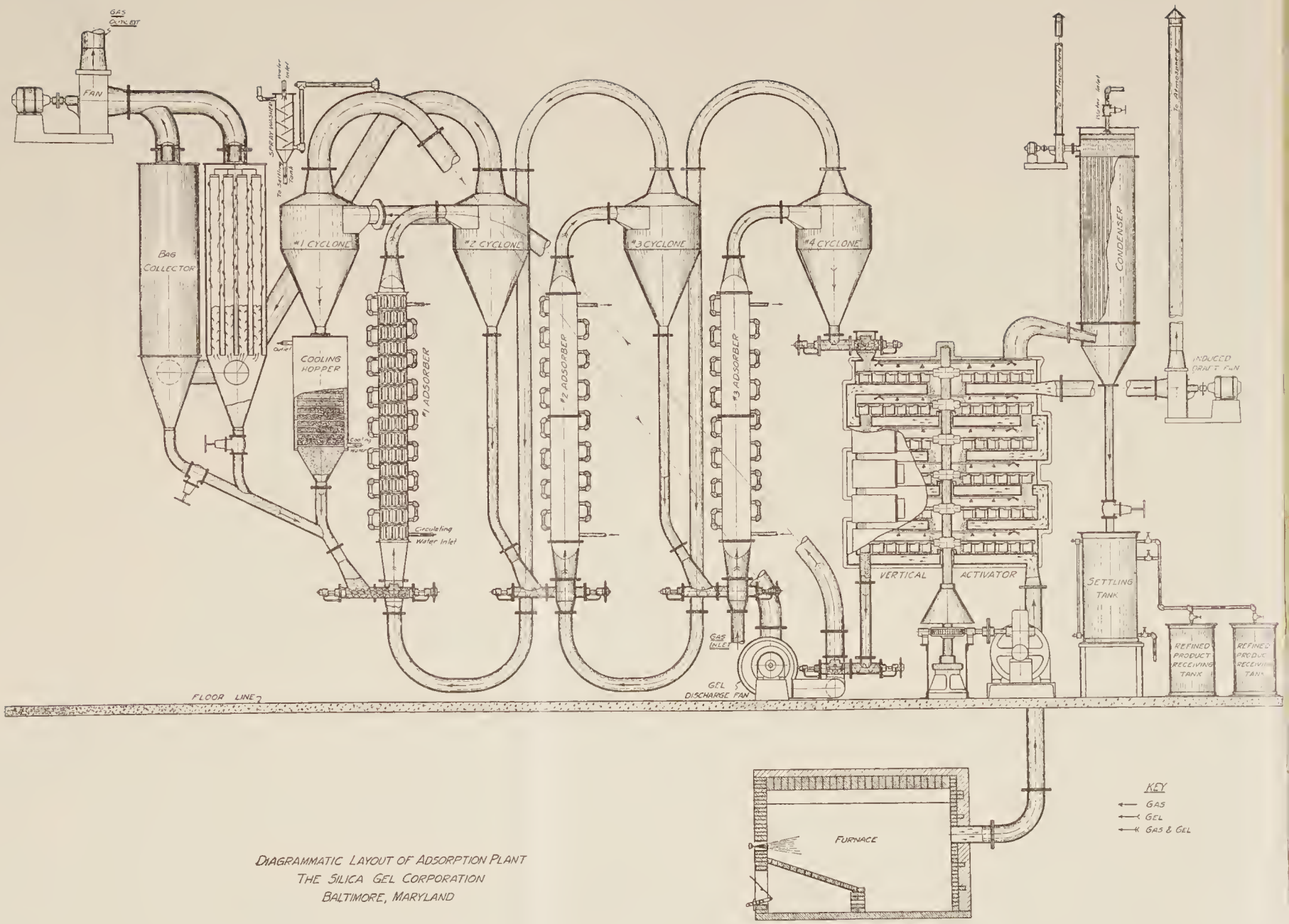



PLATE No. 1. Flow Sheet for Gas Adsorption Plant




DIAGRAMMATIC LAYOUT OF ADSORPTION PLANT
THE SILICA GEL CORPORATION
BALTIMORE, MARYLAND

PLATE NO. 2. Diagrammatic Layout of Adsorption Plant.

of screw feeders, which discharge the gel into the upward moving gas stream at the base of each of the three adsorption chambers as indicated. The velocity of the gas is such as to carry the pulverized gel along with it through the adsorption chambers, which consist of a nest of water-cooled tubes. These tubes serve the double purpose of thoroughly mixing the gel and gas, in addition to their principal function of removing the heat resulting from the liquefaction of the gas being adsorbed in the pores of the gel.

The gas mixture, with the gel still in suspension, discharges from the top of each adsorption chamber into a cyclone separator, where a separation of the gel from the gas is effected. The gel so separated falls down by gravity to a screw feeder immediately beneath, which in turn discharges into the gas entering the next adsorption chamber to the right. The gas leaving the cyclone is conveyed, by suitable pipe connections, to the next adsorption chamber to the left. It is thus accomplished that, considering the entire system of adsorption chambers collectively, the gel and gas move through the plant in opposite directions; the gel moving to the right, the gas to the left.

In each adsorption chamber, as the gel moves from left to right through the plant, the saturation of gel with respect to the gas being adsorbed increases, until maximum saturation is attained in the last chamber to the right, where it meets the incoming gas. The gas, on the other hand, passing from right to left, is becoming more and more stripped of liquefiable constituents in each adsorption chamber, and leaves the system after contact with the incoming activated gel in the adsorption chamber on the extreme left. The exit gas passes finally through a tubular type of dust collector (see Plate No. 2), which recovers all the gel not separated out by the last cyclone. Such recovered gel is then returned to the system as shown.

The saturated gel is discharged from the last cyclone on the right directly into a multiple-hearth, muffle-heated activator, which is in nearly every respect similar to standard ore-roasting furnaces. The temperatures required are, however, much lower and make it possible to use an all-metal construction with asbestos insulation on the outside. The combustion gases used for heating this activator do not come in direct contact with the gel itself, so that the product adsorbed previously by the gel may be recovered from it in a practically pure state. Plate No. 2 shows a typical flow-sheet for the

recovery of gasoline from natural gas—hence the condenser into which the gasoline vapors from the activator are discharged. After the gel has passed downward through all the hearths of the activator, it is completely restored to its original condition and is ready to be returned to the starting point. This is very satisfactorily accomplished by means of a blower, which is in closed circuit with a cyclone separator located over the cooling hopper at the left of the plant.

The equipment described above has been used for a great variety of problems and is, so far as we can determine, equally well adapted to practically all industrial applications involving

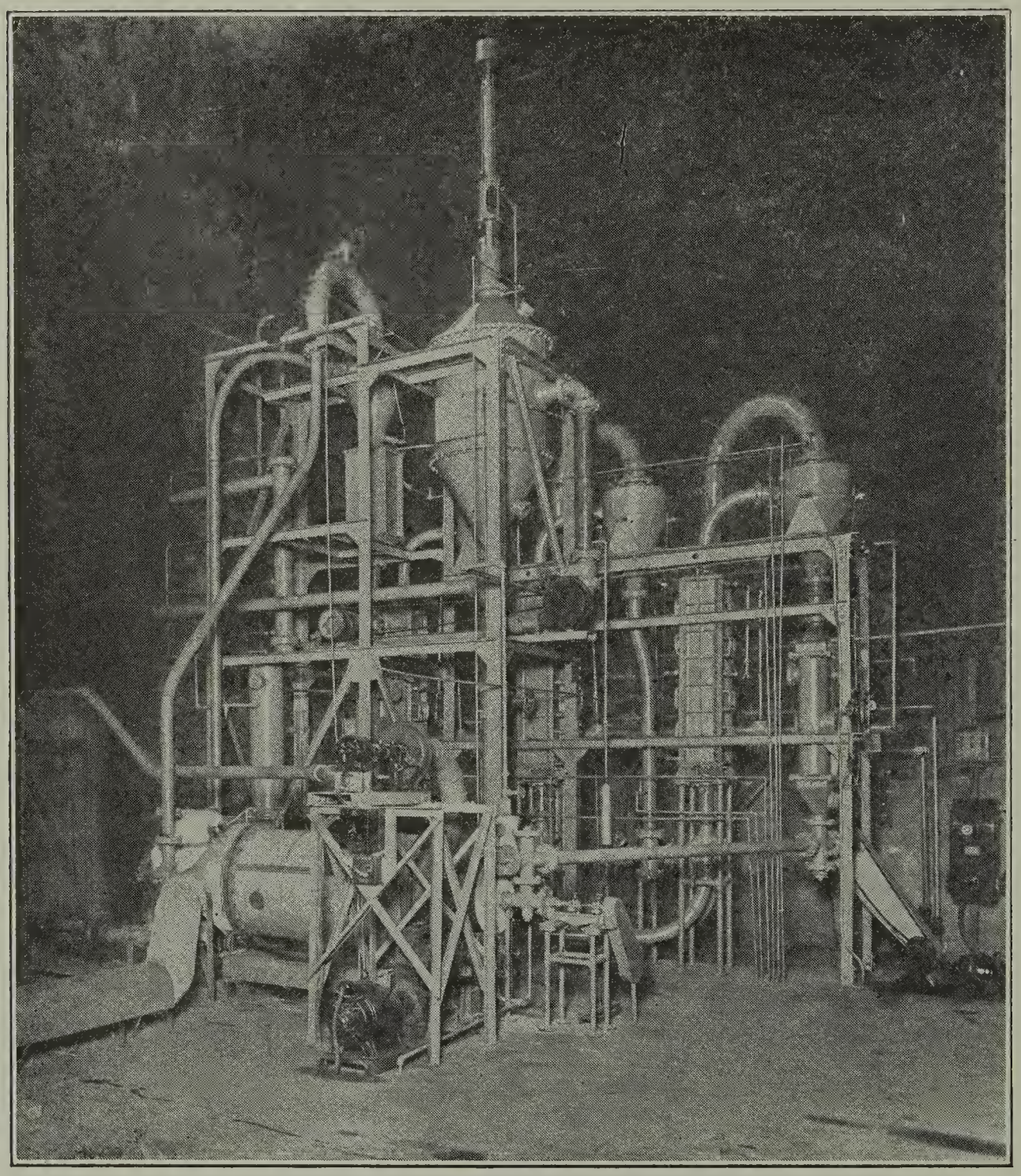


PLATE NO. 3. Silica Gel Adsorption Unit

the recovery or removal of a liquefiable gas or vapor from a mixture of gases.

Plate No. 2 is a general drawing of an adsorption unit giving more complete details of its various integral parts. The foregoing description of flow-sheet applies as well to this drawing.

Plate No. 3 is a photograph of an adsorption unit recently finished, having a capacity of 150,000 cubic feet of gas per day.

## Oil Refining Plant

For the refining of liquids, it is essential that the gel be pulverized to about 200 mesh, for otherwise the time required to reach maximum saturation with respect to the impurities being removed from a given distillate would be so great as to be prohibitive from a practical standpoint.

A study of the flow sheet illustrated in Plate No. 4 will show that in this case also we have employed a continuous and counter-current scheme of bringing the gel and liquid to be treated into contact. This is accomplished by an arrangement of standard types of mechanical agitators and rotary vacuum filters. The Oliver vacuum filter and the Bethlehem Foundry and Machine Corporation agitator have been employed in all of our work to date. This equipment is so arranged as to give intimate contact between the gel and oil, in three distinct stages, and thereafter to effect a complete separation of the two. The crude oil enters the system at the right and is thoroughly mixed with gel in No. 1 agitator. The mixture flows into No. 1 filter tub, where the gel is picked up on the surface of the filter drum, which is covered with a cloth, and the oil is sucked through the cloth into the interior of the drum. The drum is moving clockwise, and the gel cake is scraped off as shown, so that the process of separating the oil and gel is continuous.

The oil or filtrate so obtained is advanced by means of the small centrifugal pump (shown connected to the drum of the Oliver filter) to the agitator in No. 2 stage, where it is again thoroughly mixed with gel that is discharged from No. 3 filter. The mixture of oil and gel is discharged into the tub of No. 2 filter, where the gel and oil are separated by the suction of the latter through the filter cloth, similarly to the operation in No. 1 stage. The gel scraped off the drum in this stage enters the agitator in No. 1 stage, so that the mechanical action is the same for each stage. The oil to be refined is therefore being advanced by successive

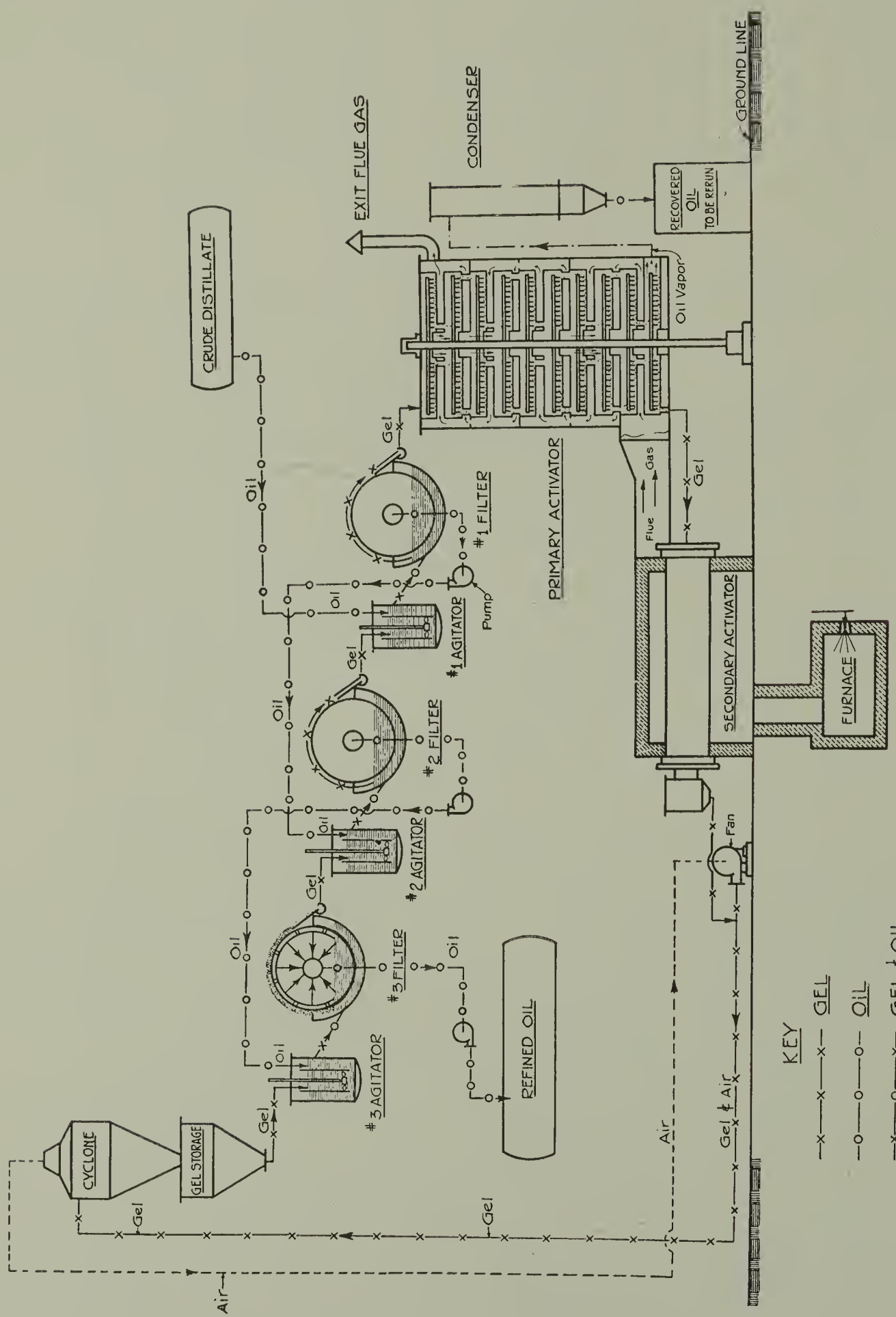


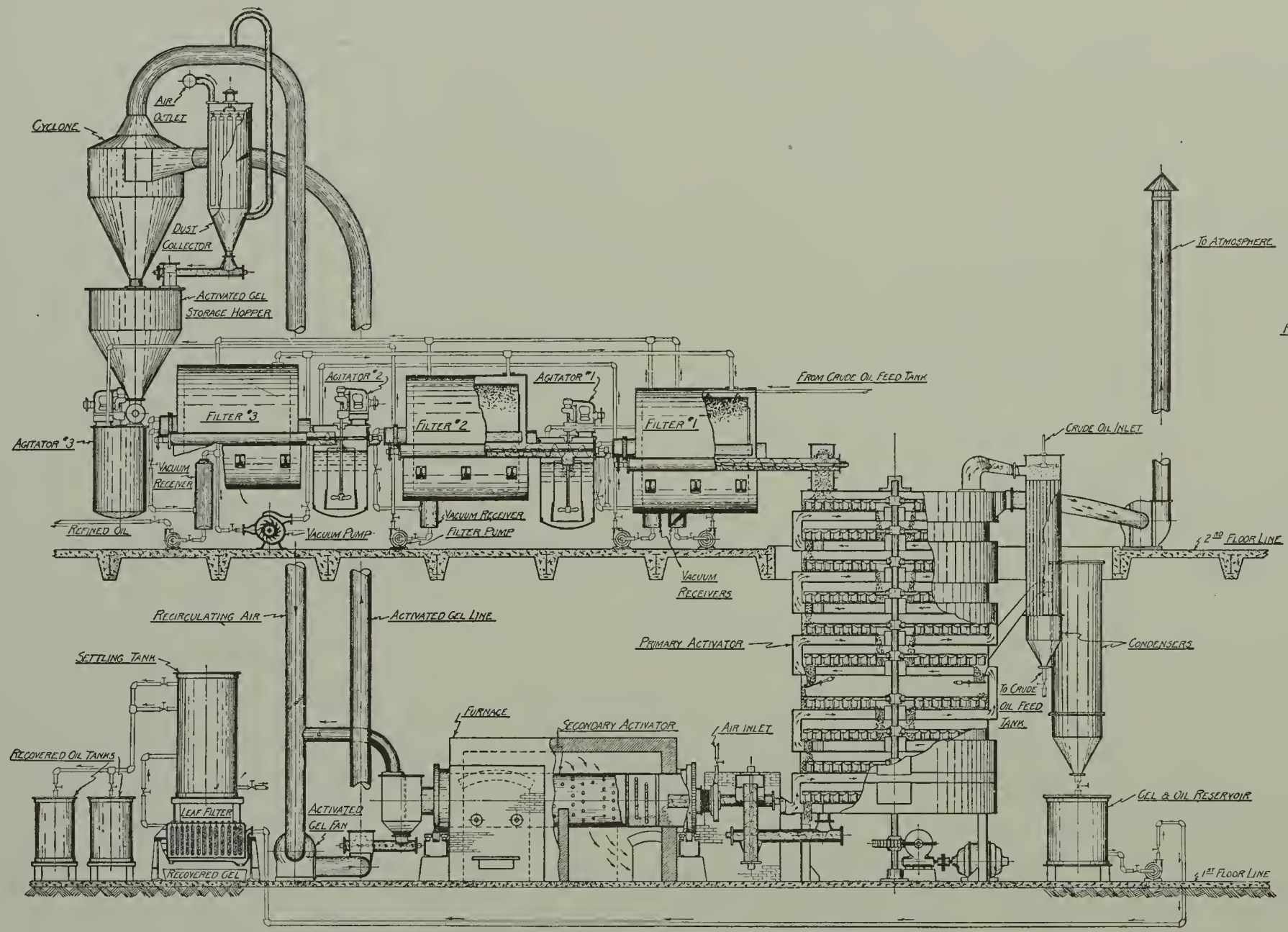

PLATE No. 4. Flow Sheet for Oil Refining Plant

stages to the left through the plant, whereas the gel starts at the extreme left and progresses toward the right, counter-current to the direction of the oil. The gel discharging from the right-hand filter is therefore saturated with impurities, whereas the liquid discharging from the left-hand filter has been completely refined.

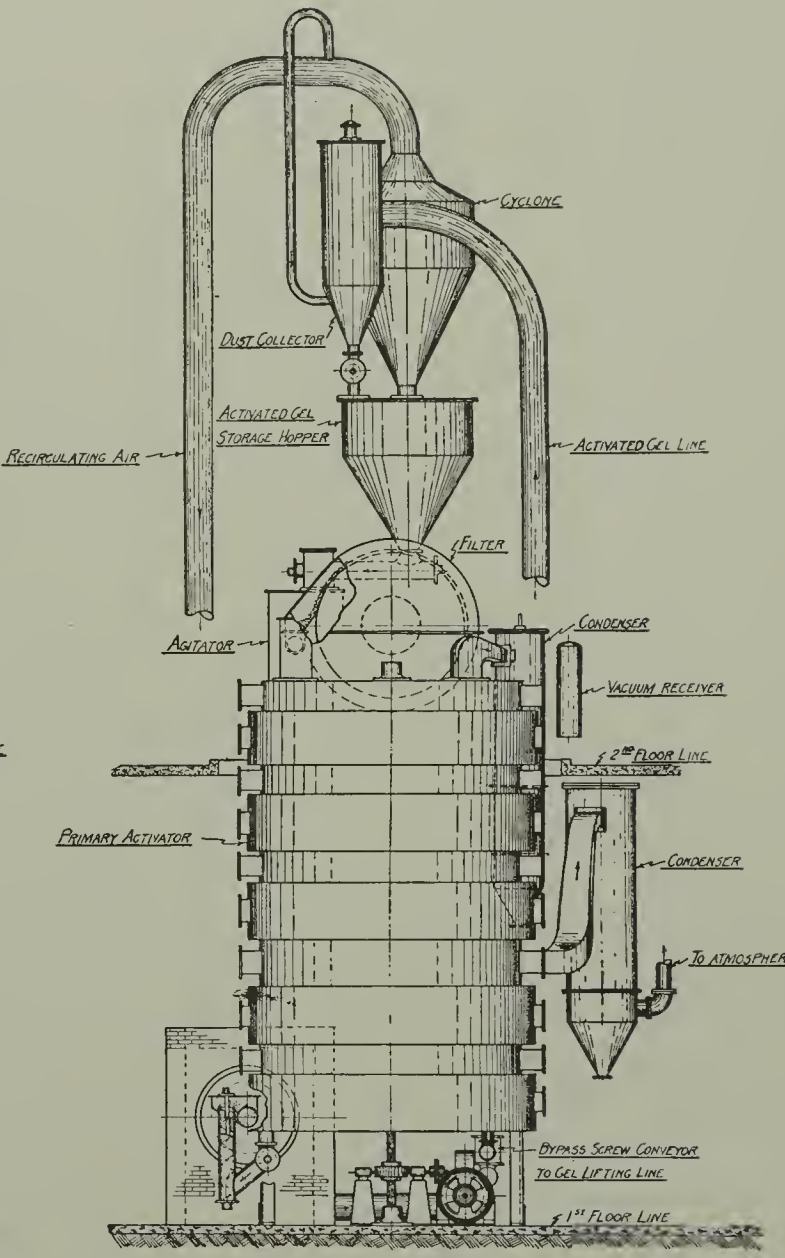
In refining petroleum oils, the activation of the saturated gel is done in two stages. The primary activator is a multiple-hearth, muffle-heated type, similar to the one before described in connection with the gas adsorption plant. The function of this primary activator is the practically complete removal and recovery of all oil in the pores of the gel, together with the small percentage of free oil wetting the exterior of the gel particles. The oil so recovered is condensed in the condenser shown connected to the activator, and may be further refined or disposed of in any manner desired.

The gel discharged from the bottom of the primary activator contains only a trace of the oil originally present, but is usually somewhat darkened in color by the impurities of the crude oil. In the case of highly cracked gasoline, a certain amount of polymerization of gum-forming compounds takes place in the primary activator, leaving a small percentage of the same on the surface of the gel. We, therefore, found it necessary, in order to maintain the full efficiency of the gel, to use a secondary activator, whose function it is to burn off the small residue of oil or gums that may be still adhering to the surface of the gel particles. This secondary activator is a simple steel cylinder rotating within a brick combustion chamber, and so arranged as to utilize the high temperature combustion gases, which are thereafter used to supply heat to the primary activator. A very small amount of air is admitted along with the gel entering the secondary activator, so that complete combustion of the carbonaceous matter may be effected during the gel's passage therethrough. The completely activated gel is discharged from the secondary activator into an air lifting system similar to that described for the adsorption plant, thereby completing the circuit of the gel back to its original starting point.

Plate No. 5 shows the general layout of a complete refining plant with a capacity of 3500 barrels per day. This plant is eighty-eight feet long and twenty-eight feet wide, and occupies therefore a relatively small floor space compared to its capacity. Units up to five thousand barrels per day have been completely designed




Side Elevation




End Elevation

Over all Dimensions
Height 66-Ft.
Width 28 "
Length 88 "

PLATE NO. 5. Silica Gel Oil Refining Plant.

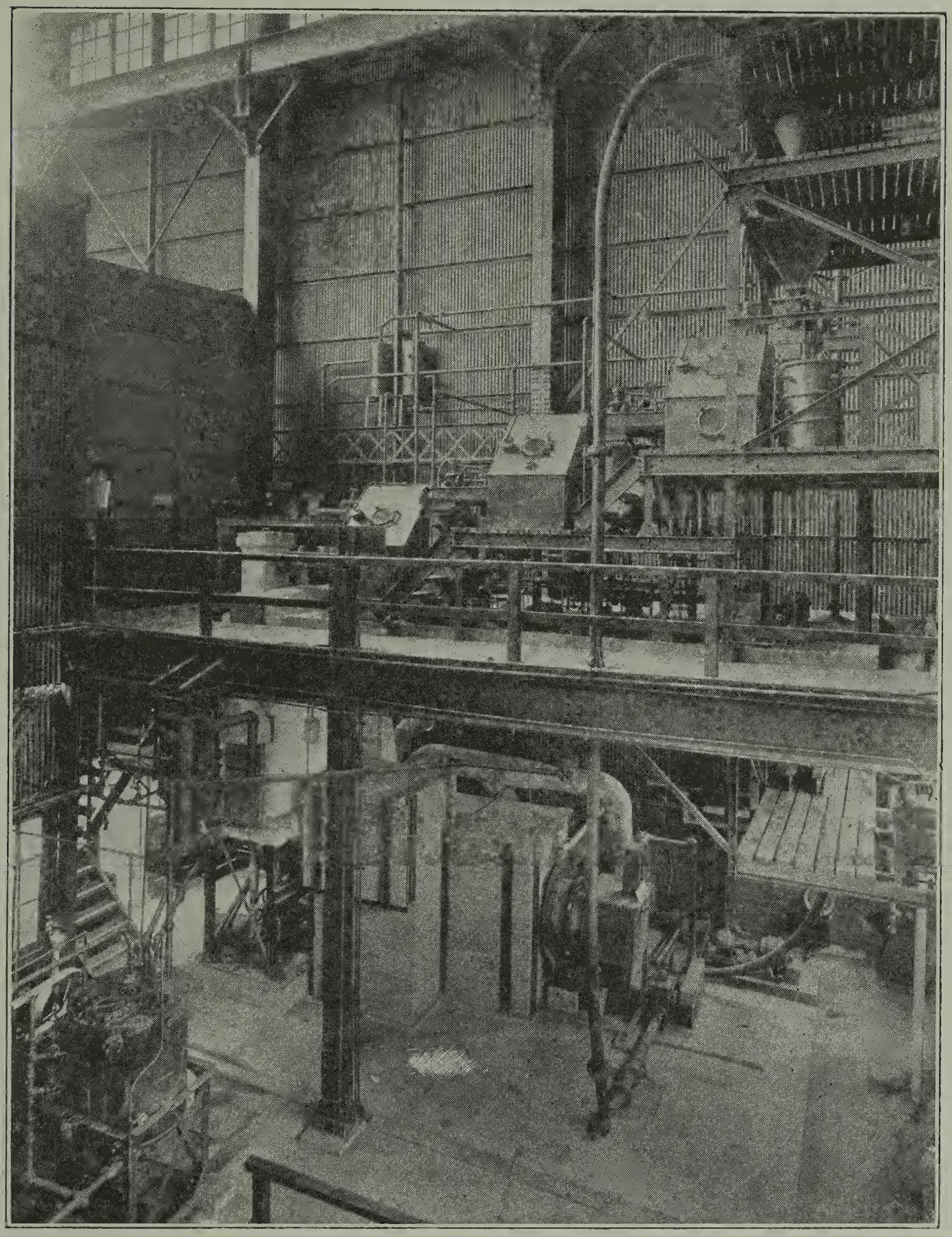


PLATE NO. 6. Silica Gel Oil Refining Plant
Equipment for Refining on Upper Floors, Apparatus for Reactivating Gel on Ground Floor. Cycle of Operation Continuous

and require very little more room than the above mentioned three thousand five hundred barrel unit.

Plate No. 6 is a photograph of the refining unit now in operation at the plant of The Davison Chemical Company, Baltimore, Md. Plate No. 7 and No. 7-A show in more detail the upper and lower portions of the same plant.

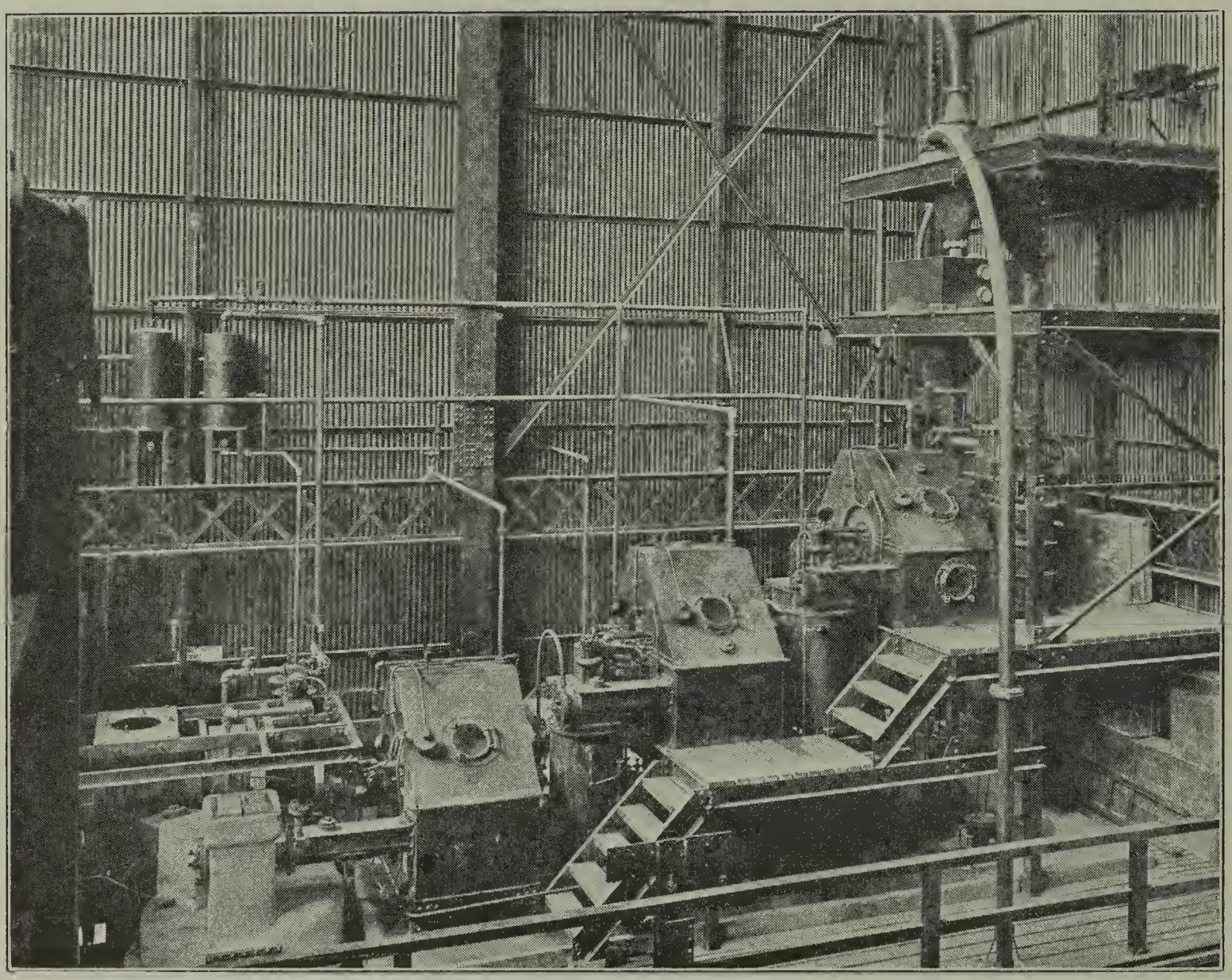


PLATE NO. 7. Cascade of Agitators and Filters Constituting Refining Plant

## OIL REFINING

There are two very different and distinct operations that go hand in hand in the complete processing of crude oil by the refiner.

The first has to do with dividing up the original crude by distillation into the well known fractions, gasoline, kerosene, lubricating oil, etc., in accordance with their respective boiling points. This is accomplished by fractional distillation, and is capable of endless variety as to character of apparatus used and products obtained.

Distillation of the lighter fractions from crude oil is carried out in what may be termed primary stills. These have, until very recent years, been of the batch type, and no great care was taken to equip them with efficient fractionating columns, since only a rough cut was made, with the idea that after chemical treatment of the original distillate a final and more careful distillation would be made

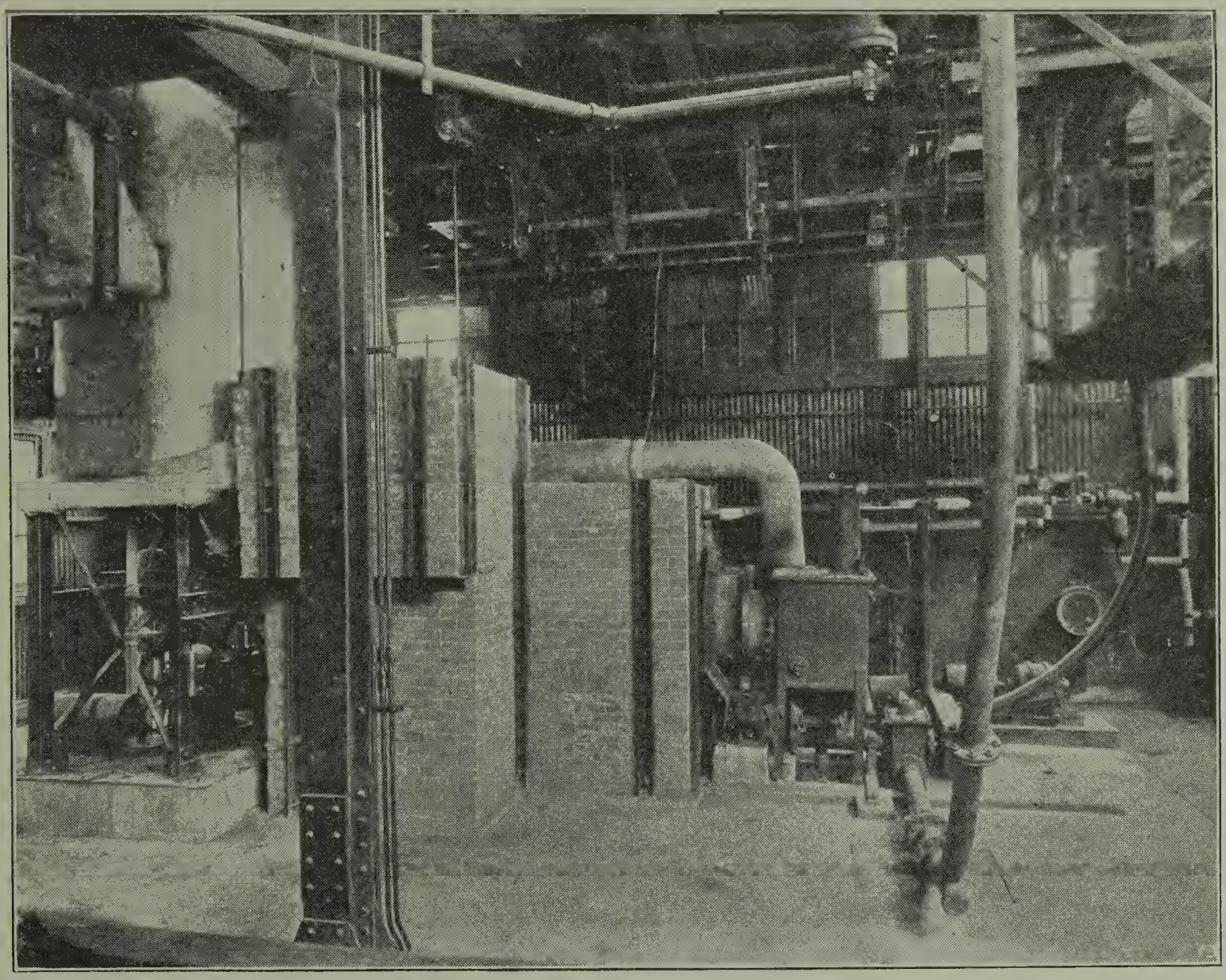


PLATE No. 7-A. Vertical and Horizontal Activators for Restoring Efficiency of Silica Gel

to obtain gasoline of exact boiling point range. Gasoline therefore, as now refined, undergoes two complete distillations to obtain a finished product: one in the original or primary still; the second, after chemical treatment, in what is known as the re-run or steam still.

It is apparent, therefore, that one of the two distillations mentioned is occasioned by and supplemental to the chemical treatment

to which the distillate is subjected during the refining process. The necessity for this second distillation grows out of the formation of asphaltic compounds, resulting from chemical reaction between the sulphuric acid used and unsaturated hydrocarbons present in the distillate being treated.

Any incentive to make a final cut of gasoline on the primary stills is therefore lacking so long as a subsequent distillation after chemical treatment is a necessary part of the refining process.

In the case of kerosene it has likewise been customary to finish the refining operation with a steam distillation, so as to leave behind in the still all the objectionable compounds produced by treating the oil with sulphuric acid. It may thus be seen that distillation has in the past been so interwoven with chemical treatment of oils that the two have been inseparable companions.

When we speak, therefore, of refining petroleum oils in terms of existing practice, we must figure on distillation after treatment as a most necessary step in such process.

## Definition of "Refined" Oils

Before entering upon the discussion of a physical means of refining oils as contrasted to the chemical method above mentioned, we should first endeavor to define just what is meant by "refined" oil. It almost goes without saying that gasoline, kerosene, and lubricating oils must be of a color and odor that please the consumer of these products. In the case of kerosene, a poor product is apparent to the user very soon after he starts to burn it in his lamp. He cannot tell, however, either by its appearance or its odor when purchase is made, whether or not it will prove satisfactory in actual use. Also in the case of gasoline, the retail buyer is equally helpless to judge, nor does he know what to specify as a desirable gasoline, aside from appearance and odor. Here again we may have a beautifully white product, and one of pleasing odor, which, however, may be of very inferior quality, so far as its actual performance is concerned. Much study has been given both by refiners and automotive engineers to the question of distillation characteristics of motor gasoline. This has been a most important study, since it has directly to do with increasing, from a given crude oil, the quantity of gasoline that may satisfactorily be used in the automobile engine. This is, however, a purely thermodynamic problem, and even when completely solved to the entire satisfaction of everybody concerned,

including the public, does not in any degree disclose, nor even suggest, necessary *quality* standards of refining. It is quite possible to produce a motor gasoline which may satisfactorily fulfill the requirements of odor, color, and proper distillation range, and yet be in reality an unrefined product.

It is equally possible to produce a lubricating oil of attractive color, proper viscosity, and conforming to all the physical specifications customarily used, that nevertheless will fail when put to the actual service test.

What is there in petroleum oils, in the way of impurities, that must be removed before they earn the title of "refined" products? The answer is, of course, sulphur.

What is it, for instance, that differentiates high grade Pennsylvania gasoline, kerosene and lubricating oil from the corresponding products obtained from Mexican crudes? It is nothing more or less than the respective amounts of sulphur present in these two crudes. Remove the excess sulphur from the Mexican distillates, and in each fraction so treated you will have a finished product in all respects the equal of the best that can be obtained from the purest Pennsylvania stock. This statement is made as the result of an intensive study for over three years, in which distillates from crudes of every known variety have been treated for the complete removal of sulphur by silica gel. This work has definitely established the fact that whenever an oil falls short of meeting the requirements of the various uses to which it is customarily put, this failure is due entirely and solely to an excess sulphur content, and may always be corrected by the removal of such excess.

This is no longer a mere theory or matter for speculation, since it is now possible with silica gel actually to effect a complete removal, if necessary, of all sulphur from any oil under discussion. It is consequently possible, for the first time, actually to demonstrate the correctness of this statement, since heretofore chemical means of removing sulphur from high sulphur distillates was the only method available, and was so inherently inadequate that only partial removal was actually attained. With silica gel as a means of complete separation of sulphur compounds from the pure hydrocarbons present, we are able, in each case, to observe the behavior of an oil free from sulphur.

We shall therefore endeavor to show that we ought to think of oil refining in terms of sulphur content, since this has in every case

proved to be the only factor that can logically be said to influence the actual behavior of the various petroleum fractions.

## The Silica Gel Process of Refining Versus Acid Treatment

The selective adsorption by silica gel of sulphur compounds from the crude distillate is a purely physical phenomenon and consequently leaves no products of chemical reaction in the oil to be later removed by distillation. We have therefore eliminated the necessity for distillation after treatment as one of the steps in refining, and thereby not only save the actual cost of the same, but avoid also the accompanying distillation losses. The physical removal of sulphur compounds by silica gel leaves the distillate so treated absolutely neutral chemically and entirely free from the objectionable polymerized products that result from the action of sulphuric acid on unsaturated hydrocarbons. This is especially important in the case of cracked gasolines and distillates from crudes, high in aromatic forms of hydrocarbons. The California oils are typical examples of the latter, and have presented to the refiner problems that have not been economically solved by chemical methods of refining. The fatal defect of sulphuric acid as a means of removing sulphur impurities from oils lies in its utter lack of discrimination between the perfectly good unsaturated hydrocarbons present and the sulphur compounds whose removal is desired. If, for instance, we had a cracked gasoline distillate containing 0.25 per cent sulphur, and 20 per cent unsaturated hydrocarbons, and decided to attempt the complete removal of the sulphur by treatment with sulphuric acid, we could not attain our object until most of the 20 per cent of unsaturated hydrocarbons were destroyed by reaction with the acid. This would mean a shrinkage in volume of the oil being treated that is prohibitive. It is therefore customary, when acid treatment is used, to effect only a partial removal of the sulphur impurities, since a more complete extraction would result in very great loss to the refiner.

In the days when low sulphur crude oils were sufficiently abundant to meet all demands, the refiner could produce a fairly low sulphur product without a heavy acid treatment of his crude distillates. Gasoline derived from Pennsylvania crudes, or from the better Mid-continent grades, will average as low as 0.03 per cent sulphur, even before refining. It is obvious that a very light chemi-

cal treatment is sufficient to prepare such a distillate for the market. Unfortunately, however, such high grade crudes form a comparatively small proportion of the total now required for the immense demand created by the modern use of automobiles. Most of the new crude oil production is of the higher sulphur type, and is confronting the refiner with a problem which, it is our belief, cannot properly be solved by chemical means.

Further, to complicate the problem, the great increase in the proportion of gasoline made by cracking processes has resulted in a distillate to be treated that is not only high in sulphur, but contains unsaturated hydrocarbons which, as described above, react with the very sulphuric acid that is aimed primarily at the removal of the sulphur compounds present.

It has been thought, heretofore, that unsaturated hydrocarbons, even though free from sulphur impurities, were undesirable constituents of kerosene. They were held responsible for the smoky burning of cracked kerosenes, and little attempt has been made to utilize the kerosene fraction resulting from the cracking of heavy oils. We have conclusively shown, however, that owing to the impossibility of complete removal of sulphur from such cracked products by chemical treatment, without a simultaneous elimination of the unsaturated compounds originally present, it was never possible actually to determine whether the sulphur or the unsaturated hydrocarbons were to blame.

With the aid of silica gel as a means of complete removal of sulphur from such cracked products, without the corresponding elimination of the unsaturated hydrocarbons, we were able for the first time to decide which is the real offender.

As will be shown by actual lamp tests on kerosene of this character, it is only necessary to effect the removal of the sulphur compounds to obtain an oil of fine burning quality, even though the percentage of unsaturated hydrocarbons is but slightly reduced.

## Effect of Sulphur Removal on Burning Quality of Kerosenes

In order definitely to establish the effect of sulphur content on the burning quality of various kerosenes, we selected the following typical kinds to study this point:

1. Mexican Straight Run Kerosene. Plate No. 8.
2. California Straight Run Kerosene. Plate No. 9.

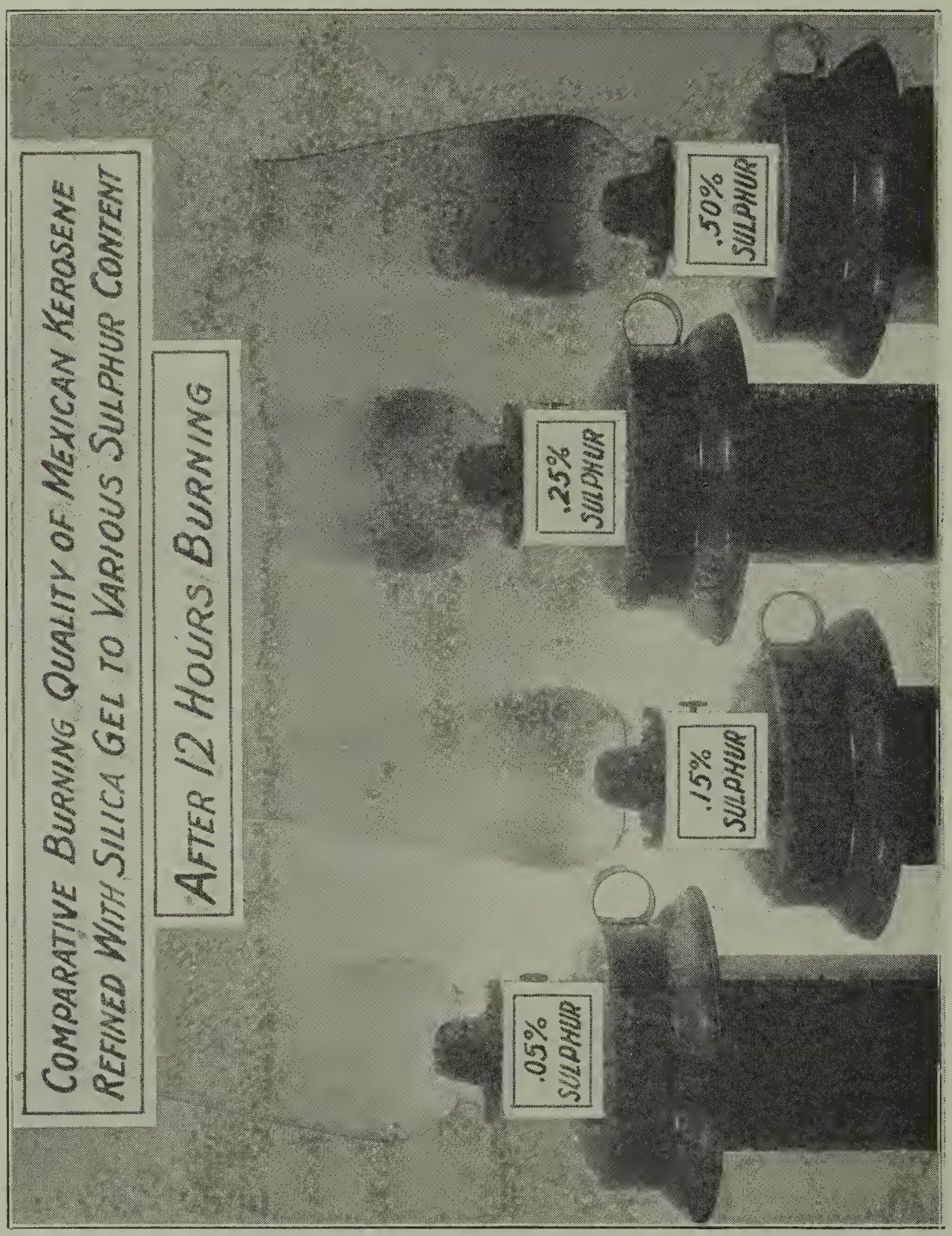

COMPARATIVE BURNING QUALITY OF MEXICAN KEROSENE
REFINED WITH SILICA GEL TO VARIOUS SULPHUR CONTENT
AFTER 12 HOURS BURNING
.25% SULPHUR
.50% SULPHUR
.05% SULPHUR
.15% SULPHUR

PLATE No. 8

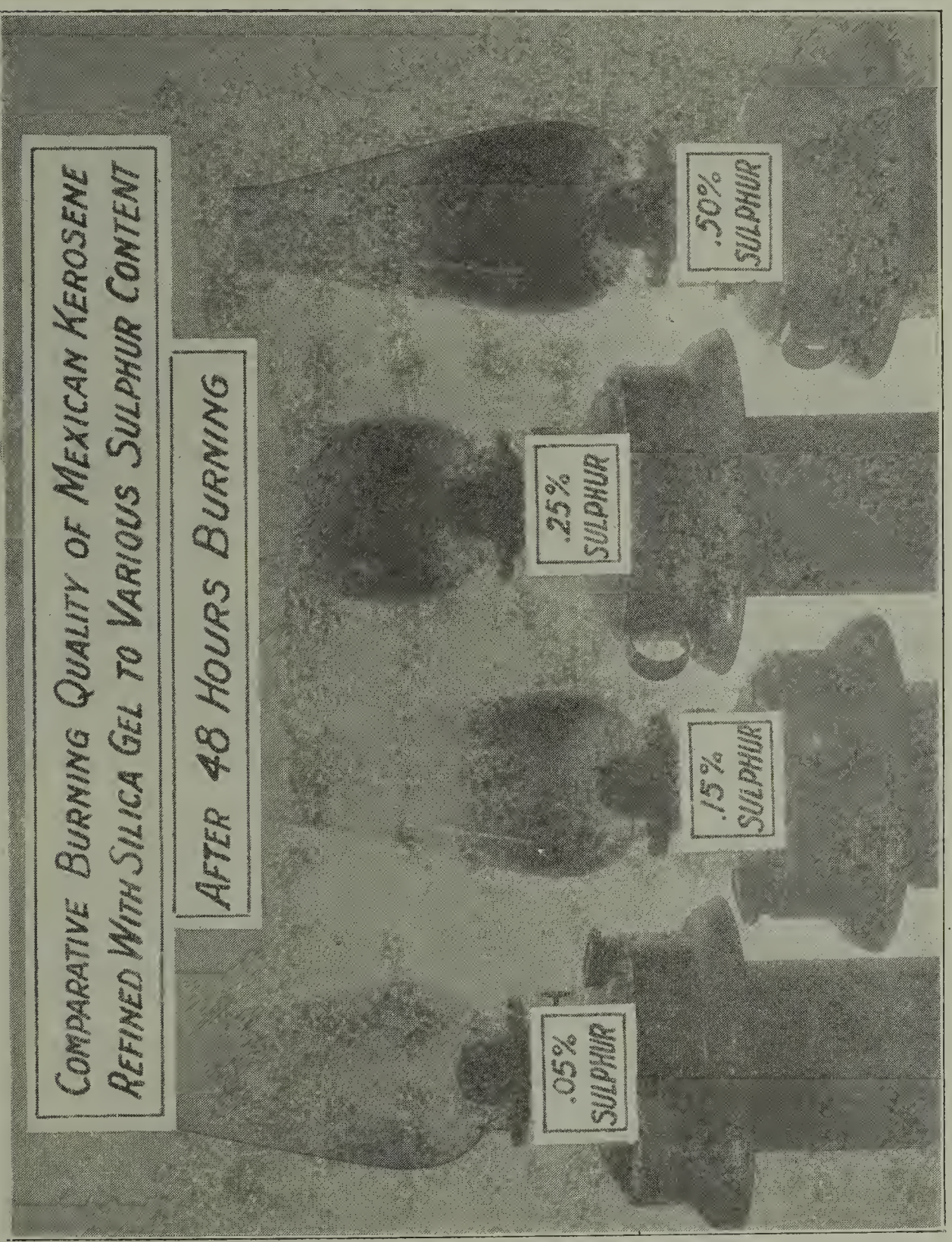

COMPARATIVE BURNING QUALITY OF MEXICAN KEROSENE
REFINED WITH SILICA GEL TO VARIOUS SULPHUR CONTENT
AFTER 48 HOURS BURNING
.25% SULPHUR
.50% SULPHUR
.05% SULPHUR
.15% SULPHUR

PLATE No. 84

Each of these distillates was obtained in its unrefined state, and four portions of each kind treated with varying amounts of silica gel, to produce kerosenes of different sulphur content.

Burning tests in lamps of standard design were made, first, to observe the smoking and frosting of the lamp chimney, and second, the condition of the lamp wick after each twelve hour test period.

The photographs herewith were taken every twelve hours throughout the tests, and need very lttle detailed description. The very marked and consistent improvement with decreasing sulphur content is so apparent as not to call for extended remarks. It should be noted, however, that in the case of the California kerosene, a much more complete removal of sulphur is necessary to obtain a product of given quality than is the case with the Mexican distillate. This is no doubt connected in some way with the different behavior of unsaturated hydrocarbons, when associated with given percentages of sulphur, as contrasted with the behavior of saturated hydrocarbons and sulphur combined in like proportions. In order, therefore, to predict what sulphur content is required for a kerosene of high quality, it must be known from what crude oil it was derived, and whether or not it has been subjected to cracking. As pointed out previously, however, it is always possible, by a sufficient removal of sulphur, to obtain a product of superior quality from any of the known kerosene distillates. We have also refined distillates of widely different gravities, and little, if any, variation in their burning quality is observed, provided in each case the sulphur content is reduced to the proper amount.

The lamp tests, illustrated by Plate No. 10, were made primarily to show the very injurious effect of an acid refined kerosene on the wick of the lamp, as compared to that of a silica gel refined kerosene of the same sulphur content. These tests, together with numerous similar ones we have made, clearly prove that when sulphuric acid is used as a means of reducing the sulphur content of petroleum products, a combination of such acid with the unsaturated hydrocarbons present results, forming compounds not completely removed by subsequent steps of the refining process. They appear to be colorless in the freshly refined distillate, and give no evidence of their presence until put to actual performance tests.

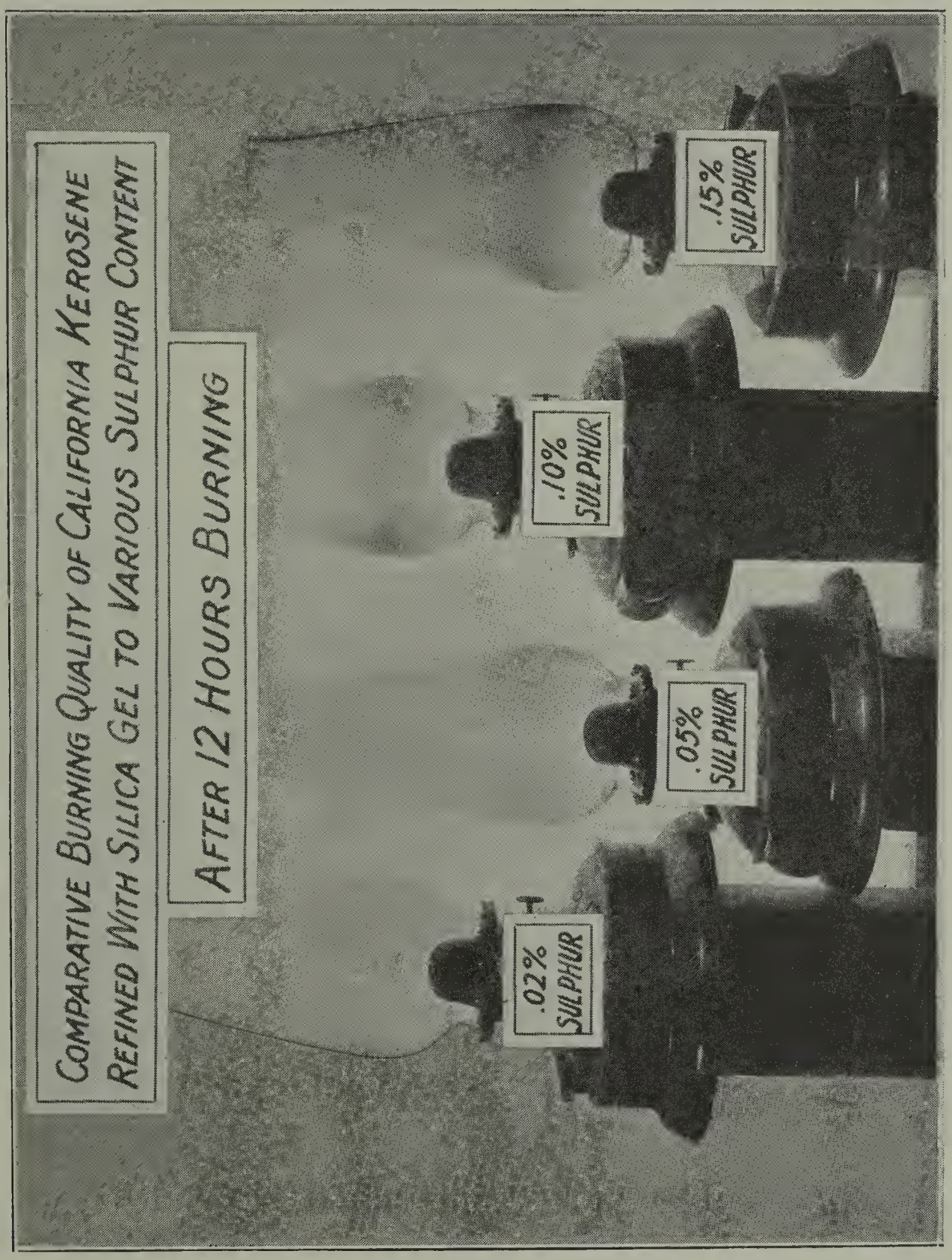

COMPARATIVE BURNING QUALITY OF CALIFORNIA KEROSENE
REFINED WITH SILICA GEL TO VARIOUS SULPHUR CONTENT
AFTER 12 HOURS BURNING
.15% SULPHUR
.10% SULPHUR
.05% SULPHUR
.02% SULPHUR

PLATE No. 9

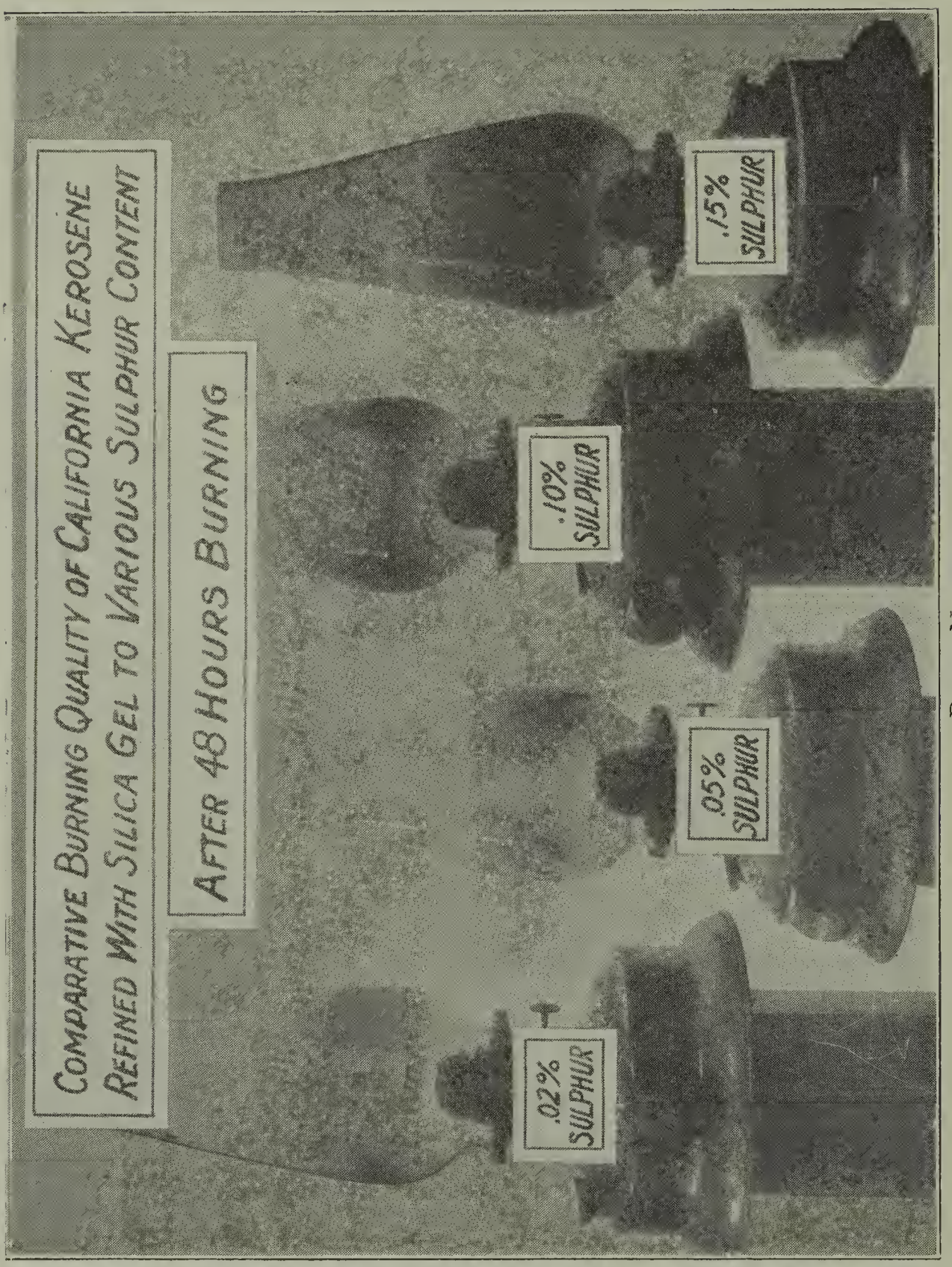

COMPARATIVE BURNING QUALITY OF CALIFORNIA KEROSENE
REFINED WITH SILICA GEL TO VARIOUS SULPHUR CONTENT
AFTER 48 HOURS BURNING
.10% SULPHUR
.15% SULPHUR
.02% SULPHUR
.05% SULPHUR

PLATE No. 9a

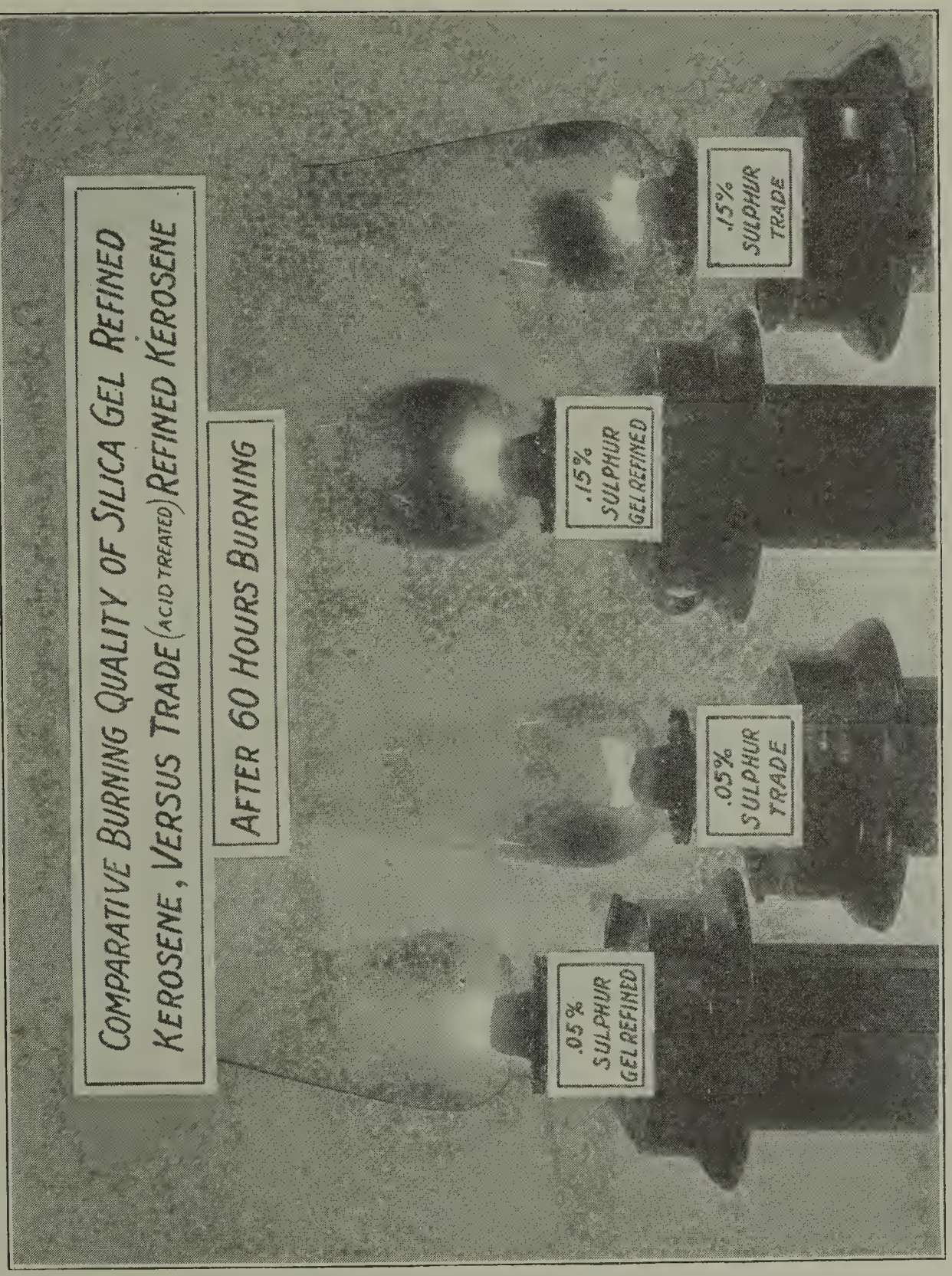

COMPARATIVE BURNING QUALITY OF SILICA GEL REFINED
KEROSENE, VERSUS TRADE (ACID TREATED) REFINED KEROSENE
AFTER 60 HOURS BURNING
.15% SULPHUR GEL REFINED
.15% SULPHUR TRADE
.05% SULPHUR GEL REFINED
.05% SULPHUR TRADE

PLATE No. 10

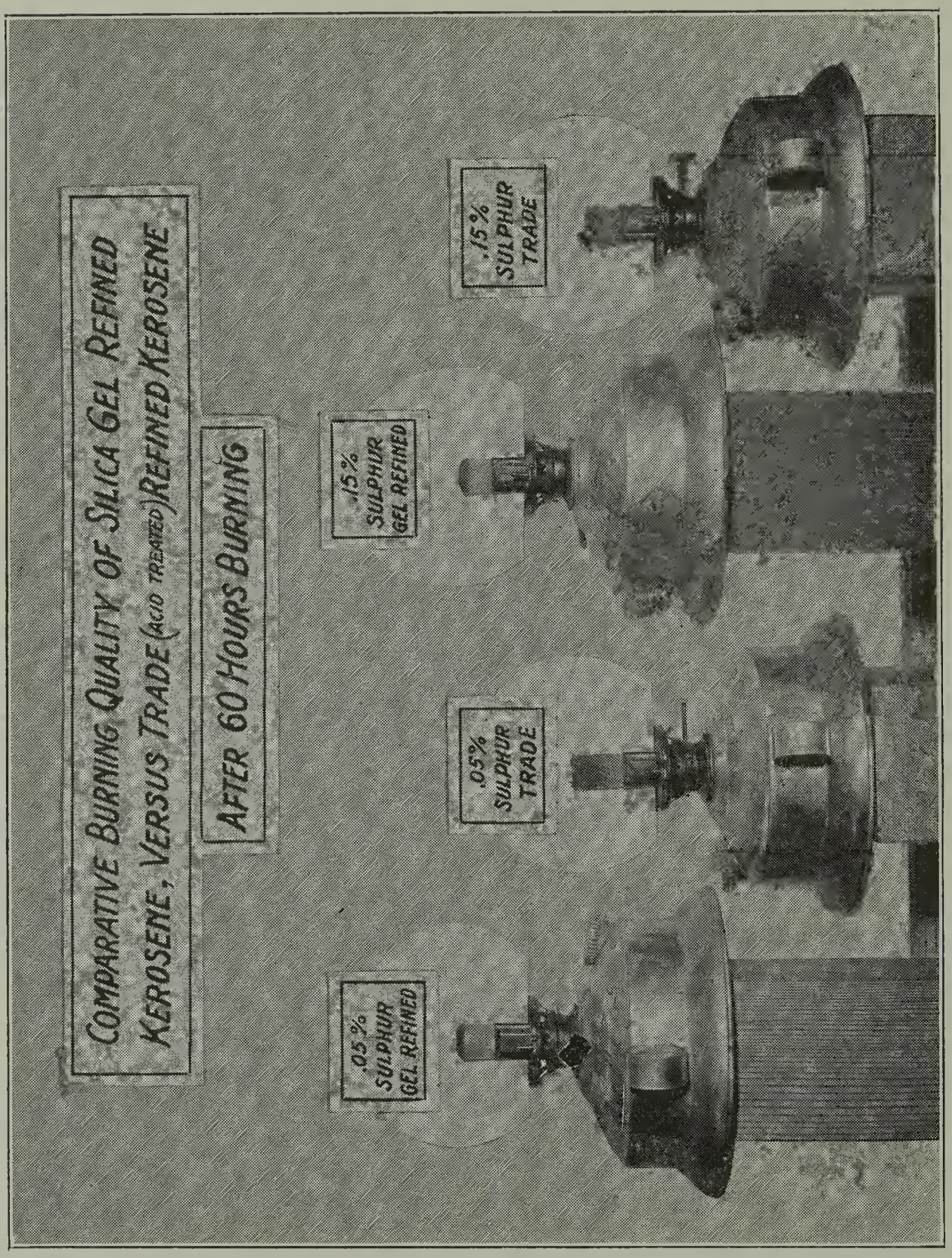

COMPARATIVE BURNING QUALITY OF SILICA GEL REFINED
KEROSENE, VERSUS TRADE (ACID TREATED) REFINED KEROSENE
AFTER 60 HOURS BURNING
.15% SULPHUR GEL REFINED
.15% SULPHUR TRADE
.05% SULPHUR GEL REFINED
.05% SULPHUR TRADE

PLATE No. 10a

## Carbon Formation in Automobile Engines

Perhaps no subject of technical nature is of more popular interest today than that of good gasoline. Every automobile driver knows that sooner or later his engine becomes fouled with carbon, to the point where its efficiency drops to such a low figure as to demand his reluctant attention to this necessary evil. He would willingly buy a higher priced fuel if by so doing the time between such cleanings could be materially lengthened. But there has been no criterion by which he could choose between the many well-advertised motor fuels so profusely offered by the well-appointed filling stations that line our principal thoroughfares and highways; nor is he quite sure whether the gasoline or the lubricating oil is most to blame for his carbon troubles. In this confused state of mind he more often dismisses the problem by blaming it on the carburetor. There is most certainly some truth in each of the three accusations, and in the hope of obtaining some practical information on this subject, we started several months ago a series of engine tests.

Our experience with kerosenes of various sulphur content naturally suggested that a corresponding improvement would also result in the case of gasoline and lubricating oils with removal of sulphur.

When planning these tests we were much surprised to find that no similar research work was recorded in the technical literature, and, so far as we could learn, the effect of various different per-percentages of sulphur compounds had not been a subject of investigation by any of the oil companies or automobile manufacturers.

We are, of course, aware of the high grade testing work carried on in the engine laboratories of the automobile manufacturers in connection with the mechanical development of their engines. It is also true that, of late, very interesting investigations have been under way to study the anti-knock characteristics of motor fuels when doped with certain organic compounds. But we have not come upon any previous instance where the relation between sulphur content of fuels and lubricating oils, and the amount of carbon formed in the engine, has been systematically studied. The data we give herewith have been checked in most cases by duplicate runs, under very closely controlled and uniform conditions. The study is by no means complete as yet, but the results so far obtained so clearly point to definite conclusions that we believe their publication is justified.

## Description of Apparatus Used

The Engine Laboratory, shown in Plate No. 11, has two separate units, one of which is used for fuel tests, the other for tests on lubricating oils. Each unit consists of a Studebaker Light-Six 1922 Automobile Engine, coupled through a Francke flexible coupling to a compound wound generator. The generator fields are either separately or self excited to enable the operator to impose heavy loads at low speeds, when desired.

The load is imposed and controlled by means of movable plates in a water box.

Number 1 Engine is used for fuel tests only. In order to compare the various gasolines, the same grade of the best obtainable lubricating oil is used in all. The carbon and gums from the cylinders and valves are carefully collected after each run and weighed.

At present we are making 200 gallon runs, which are roughly equivalent to 3,200 miles, under two-thirds full rated load at 1,000 R.P.M.

The other unit is used exclusively for lubricating oils, the tests upon which are conducted in the following manner:—

Sufficient quantity of an accepted good gasoline is obtained so that all oils are tested, using identically the same fuel. The load is maintained constant at 13 H.P. at 1,000 R.P.M.

Frequent measurements are made of volume of oil in crank case, temperature, viscosity, Baumé, sediment, etc. Additions of lubricating oil are made only when necessary to maintain normal volume in crank case.

Carbon and gum are carefully collected after each run and weighed.

It will be noted on the two charts (Plates Nos. 12 and 13) that we have endeavored to differentiate in each case between the carbon due to gasoline, and the portion chargeable to the lubricating oil. While the division is, of course, arbitrary, it is reasonably close to the truth, and serves to show, more accurately than if no attempt at division were made, the actual differences due to the gasoline alone in the one case, and to the lubricating oils alone in the other.

## Comparison of Silica Gel with Other Porous Adsorbents

In nature we meet with a number of porous materials, such as Fuller's earth, bauxite, charcoal, etc., which, when properly activated, possess to a very limited extent an internal structure similar

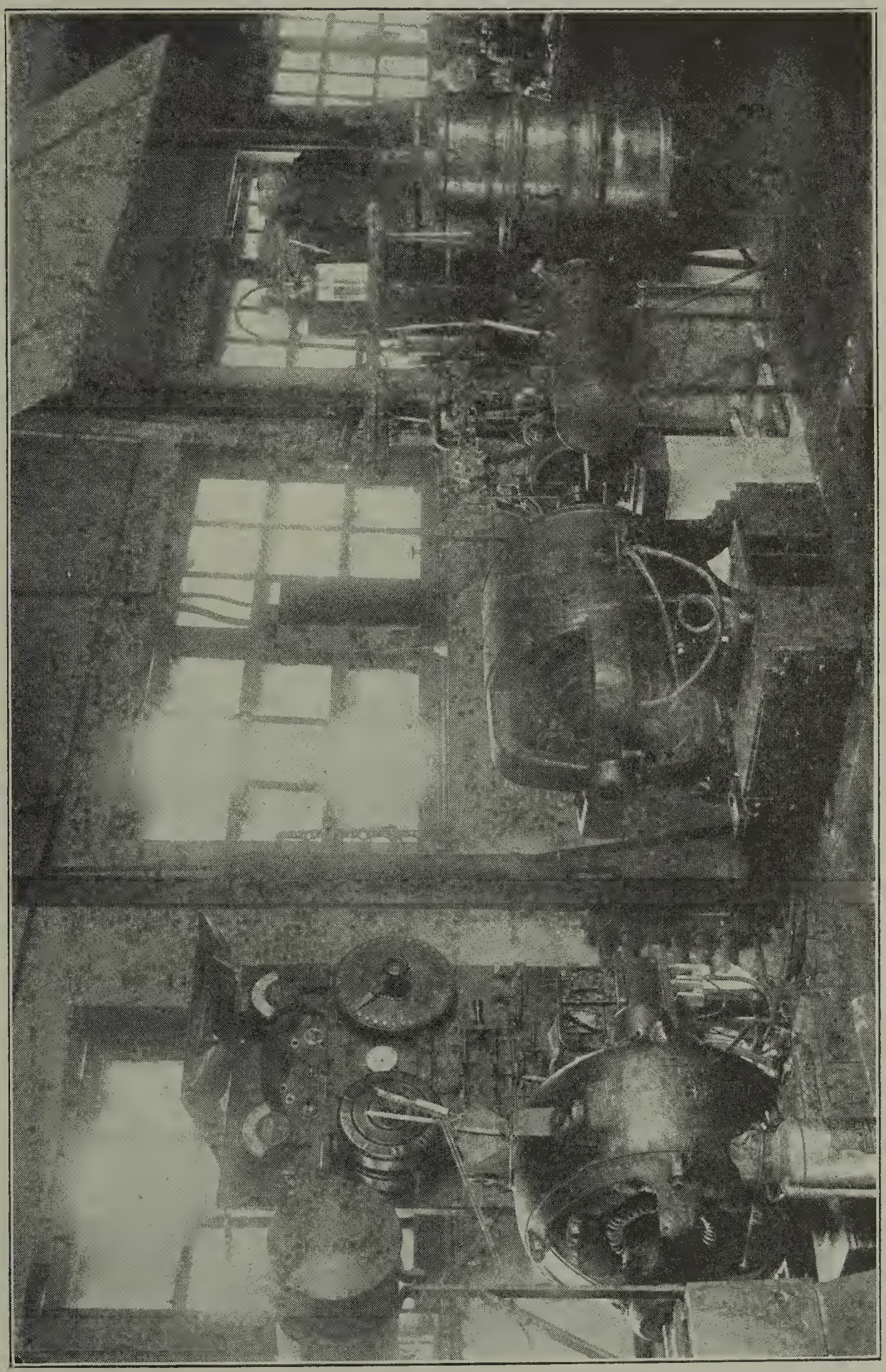


PLATE No. II

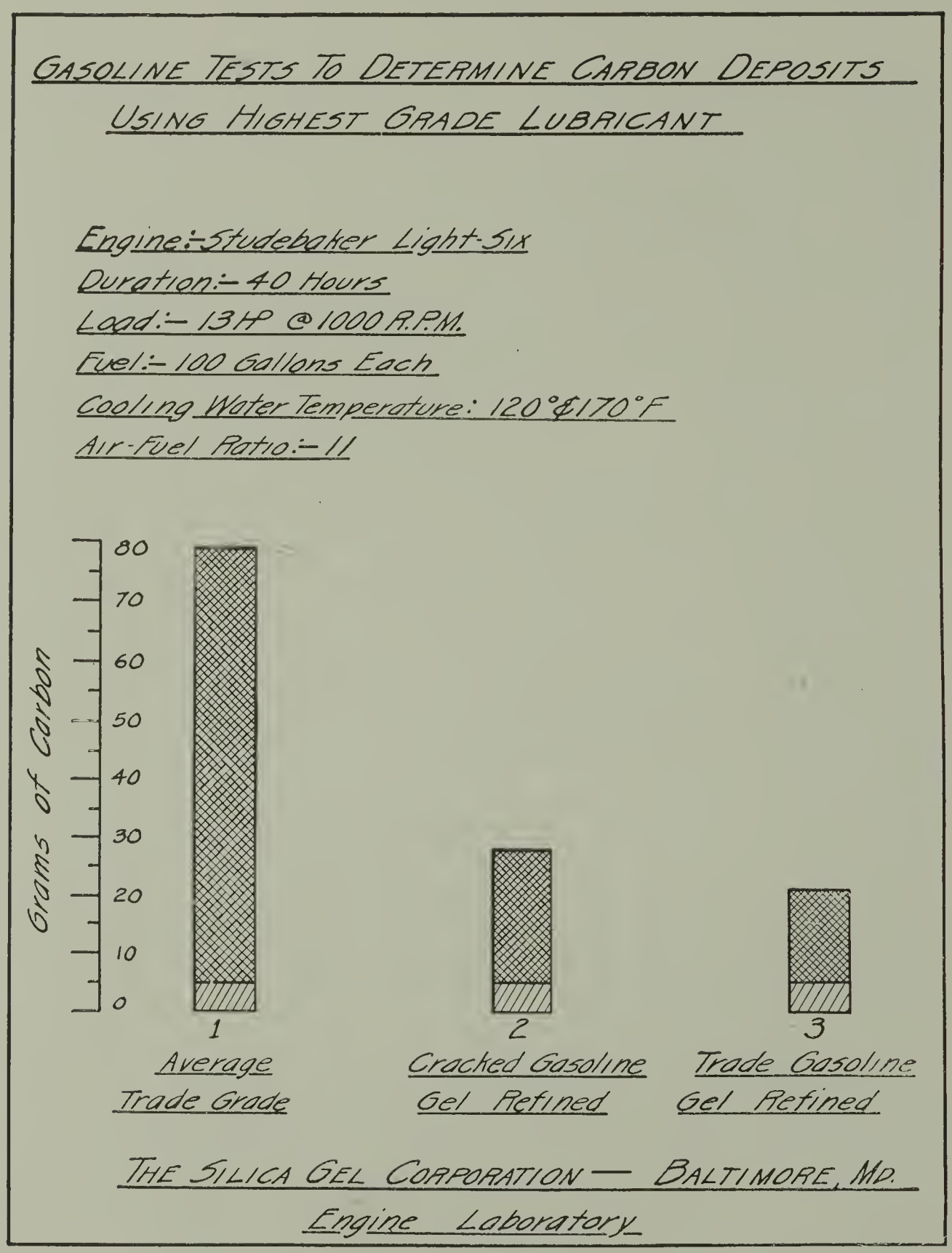



PLATE NO. 12

to silica gel. But since the exact dimensions of the pores of such materials absolutely fixes their adsorptive power, it is not to be wondered at that in nature there has not been discovered any material of just the right structure to satisfy the exacting requirements of a highly adsorptive material adapted to commercial requirements.

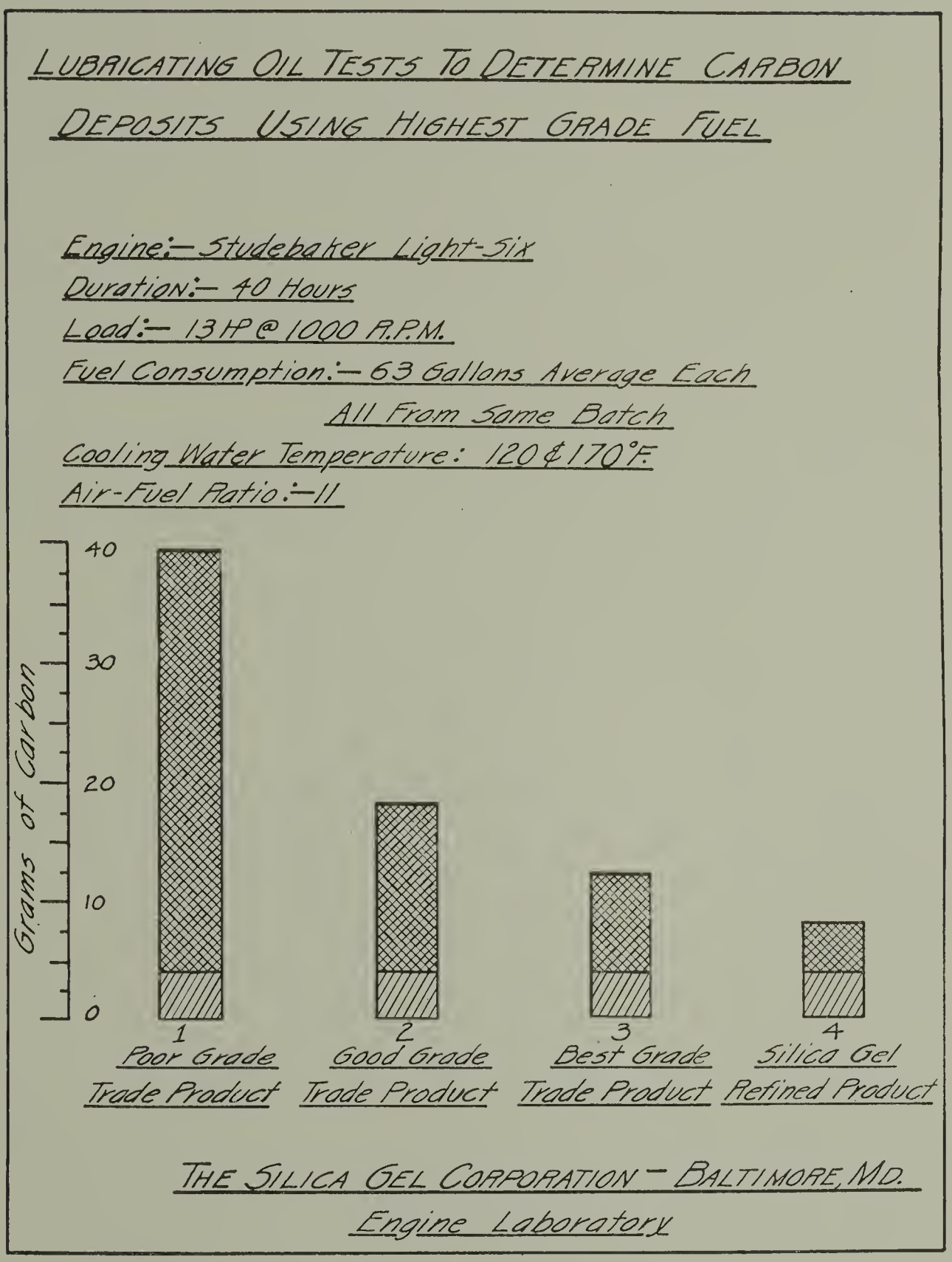



PLATE NO. 13

The natural products mentioned do all possess very marked ability to clarify liquids in which coloring matter is held in suspension. In this respect most of them are superior to silica gel. It has been shown by extensive tests we have made, however, that when materials have pores so large as to permit the ready entrance of solid particles, these pores are too large to bring about the separa-

GASOLINE TESTS TO DETERMINE CARBON DEPOSITS, USING HIGHEST GRADE LUBRICANT

| | | | Date | | |
|---|---|---|---|---|---|
| | | | December, 1922 | December, 1922 | March, 1923 |
| Time | | Hrs | 66.8 | 67.8 | 65.5 |
| Fuel | | Gal | 100.0 | 100.6 | 100.0 |
| Fuel per Hour | | Gal./Hrs | 1.50 | 1.48 | 1.53 |
| Air Fuel Ratio | | No./No | 10.95 | 10.43 | 10.90 |
| R. P. M | | | 1,000 | 998 | 1,004 |
| Avg. Water Box Load | | Watts | 8,330 | 8,500 | 8,727 |
| Output | | K. W. Hr | 636.0 | 649.5 | 648.9 |
| Thermal Value of Fuel | | K. W. Hr | 3,335 | 3,348 | 3,325 |
| Output per Gal | | K. W. Hr./Gal | 6.36 | 6.45 | 6.49 |
| Engine Intake Temp | | °F | 140 | 140 | 138 |
| Engine Discharge Temp | | °F | 170 | 170 | 169 |
| Gasoline | Initial B. P | °F | 113 | 119 | 124 |
| | End Point | °F | 433 | 401 | 436 |
| | Sulphur | Per Cent | 0.1260 | 0.0307 | 0.0380 |
| | Unsat | Per Cent | 7.90 | 20.9 | 6.0 |
| | Dish | Gum | 0.0145 | 0.0653 | 0.0050 |
| Lub. Oil | Visc. 100°F | Sec. Say | 280 | | |
| | Visc. 170°F | Sec Say | 71 | Same | Same |
| | Bé 60°F | °Bé | 29.7 | | |
| | Sulphur | Per Cent | 0.163 | | |
| Lub. Oil Consumption | | Qts | 6.25 | 6.0 | 6.6 |
| Crank Case Temperature | | °F | 170 | 168 | 177 |
| Carbon in Cylinders | | Gms | 75.65 | 25.30 | 19.57 |
| Gum on Valves | | Gms | 1.70 | 1.19 | — |
| Total | | Gms | 77.35 | 26.49 | 19.57 |
| Carbon per Gal. Fuel | | Gms./Gal | 0.7735 | 0.2649 | 0.1957 |

tion of two liquids that are in true solution. In silica gel, the preponderant proportion of the pores are of the proper size to effect the selective adsorption desired, but it nevertheless also has sufficient decolorizing properties to satisfy the strictest commercial demands in this respect.

It is obviously impossible that any material should at the same time have a structure possessing both maximum clarifying properties and maximum power to effect the separation of two liquids from true solution, since the one calls for pores of large dimensions, while the other is dependent on a structure with pores of minimum size.

The ideal material for industrial use must possess both properties in the correct proportion to accomplish the desired removal of both coloring matter and objectionable solutes.

LUBRICATING OIL TESTS TO DETERMINE CARBON DEPOSITS, USING HIGHEST GRADE FUEL

| | | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| Date | | Jan. 27 to Feb. 1, 1923 | Feb. 15 to Feb. 21, 1923 | Mar. 1 to Mar. 5, 1923 | Mar. 1 to Mar. 5, 1923 |
| Time | Hrs | 39.58 | 40.0 | 40.0 | 40.0 |
| Fuel | Gal | 65.0 | 61.5 | 60.7 | 63.5 |
| Fuel per Hour | Gal./Hrs | 1.64 | 1.54 | 1.52 | 1.59 |
| Air Fuel Ratio | No./No | 11 | 11 | 11 | 11 |
| R. P. M | | 935 | 995 | 1,002 | 1,000 |
| Avg. Water Box Load | Watts | 8,680 | 8,505 | 8,733 | 8,826 |
| Output | KWHr | 393.4 | 390.6 | 399.7 | 403.4 |
| Thermal Value of Fuel | KWHr | 2,163 | 2,048 | 2,020 | 2,115 |
| Output per Gallon | KWHr./Gal. | 6.05 | 6.34 | 6.58 | 6.35 |
| Engine Intake Temp. | °F | 121 | 130 | 123 | 130 |
| Engine Discharge Temp. | °F | 173 | 175 | 173 | 180 |
| Gasoline — Initial B. P. | °F | 133 | | | |
| Gasoline — End Point | °F | 402 | | | |
| Gasoline — Sulphur | Per Cent. | .0955 | Same | Same | Same |
| Gasoline — Unsat | Per Cent. | 6.0 | | | |
| Gasoline — Dish | Gum | .0076 | | | |
| Lub. Oil — Visc. 100°F | Sec. Say | 280 | 280 | 277 | 246 |
| Lub. Oil — Visc. 170°F | Sec. Say | 75 | 71 | — | 65 |
| Lub. Oil — Bé 60°F | °Bé | 29.7 | 29.7 | — | 25.5 |
| Lub. Oil — Sulphur | Per Cent. | .290 | 0.163 | 0.269 | 0.136 |
| Lub. Oil Consumption | Qts | 4.0 | 2.4 | 2.1 | 1.3 |
| Crank Case Temperature | °F | 167 | 174 | 163 | 172 |
| Carbon in Cylinders | Gms | 38.540 | 18.10 | 11.9946 | 7.8570 |
| Gum on Valves | Gms | .760 | — | — | — |
| Total | Gms | 39.300 | 18.10 | 11.9946 | 7.8570 |
| Carbon per Gal. Fuel | Gms./Gal. | .6045 | 0.2926 | 0.1976 | 0.1237 |

A long series of tests on petroleum oils of great variety have conclusively shown that in silica gel we have the proper balance of the above mentioned characteristics to remove color to any degree commercially required, while at the same time effecting a more complete removal of sulphur compounds than is accomplished by even the best chemical treatment now known.

We illustrate, on Plate No. 14, a chart with curves plotted to shown the relative ability of various adsorbents to remove sulphur compounds from Mexican kerosene. An examination of these data discloses the fact that none of the other materials even approximates the capacity exhibited by silica gel. In fact, the quantity of any other adsorbent required to reduce the sulphur content of this

oil to a commercial quality is so great as to preclude its use for this purpose.

For instance, if we attempt to use bauxite to make a kerosene containing 0.06 per cent sulphur, we obtain only 15 parts of such an oil from 100 parts of bauxite. There would be left in the bauxite approximately 56 parts of oil higher in sulphur than the original crude kerosene, which would constitute so great a shrinkage in the amount of finished kerosene obtained as absolutely to forbid such a procedure.

## Other Chemical Methods of Refining

There are, of course, chemical means other than sulphuric acid for the extraction of sulphur compounds; such, for example, as treatment with liquid $SO_2$, or an oxidation method, of which the sodium hypochlorite treatment is typical. Neither of these latter mentioned methods, however, avoids the objection pointed out in the case of sulphuric acid, since in both cases a removal of unsaturated bodies accompanies the extraction of sulphur. And, furthermore, in the case of a hypochlorite treatment of cracked gasoline, objectionable chlorine compounds would remain in the oil itself. It need hardly be pointed out that in attempting to refine by this method oils high in unsaturated hydrocarbons, a greatly increased consumption of chlorine would result as compared to the treatment of saturated oils.

## Increased Gasoline Yield by Silica Gel Method

We have heretofore discussed the superior quality of petroleum products, when gel refined, as compared to the same products prepared by the chemical treatment now in general use. We will now consider the phase of our discussion of more immediate interest to the refiner himself. We do not mean to suggest that the refiner is not also interested in the quality of product he turns out, but it is only natural that his greatest enthusiasm is aroused by the anticipation of greater yields and, therefore, reduced costs.

In order to measure the quantity of gasoline obtained from a given distillate, we must first define by certain distillation characteristics exactly what fraction we have in mind. The specification for New Navy gasoline has become more generally adopted, perhaps, than any other in general use, and will, therefore, be used in the present discussion. This specification stipulates a 437° F. end

COMPARATIVE YIELDS OF GASOLINE, SILICA GEL VERSUS ACID REFINING

| | Naphtha | | | Gasolines | | | | | | Bottoms | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 6 Lbs. 2½–1 | | | 70 % Cut | | | 74 % Cut | | | Crude | Acid | Gel |
| | Crude | Acid | Gel | Crude | Acid | Gel | Crude | Acid | Gel | | | |
| Gravity (Bé. @ 60°F.).... | 52.1 | 50.9 | 52.9 | 55.8 | 55.7 | 57.6 | 55.0 | 55.1 | 56.5 | 37.7 | 37.9 | 40.6 |
| Sulphur..... | .164 | .105 | .07 | .132 | .062 | .044 | .148 | .076 | .058 | .408 | .357 | .143 |
| Color..... | –9 | –7 | 18+ | 13 | 21 | 25+ | 11 | 18 | 25+ | Black | Black | Yellow |
| Doctor..... | Sour | Sweet | Sweet | Sour | Sl. Sr. | Sweet | Sour | Sl. Sr. | Sweet | Sour | Sour | Sweet |
| Unsat. (Acid Adsorpt.) . | 11.5 | 10.6 | 11.0 | | | | 11.8 | 10.7 | 11.4 | 7.0 | 7.8 | 6.0 |
| Corrosion..... | Cor. | Cor. | O. K. | Cor. | Cor. | O. K. | Cor. | Cor. | O. K. | | | |
| Distillations made by fire alone using a small column. | | | | | | | | | | | | |
| DISTILLATIONS: | | | | | | | | | | | | |
| Initial..... | 109°F. | 127°F. | 133°F. | 124°F. | 131°F. | 127°F. | 131°F. | 135°F. | 133°F. | 419°F. | 421°F. | 415°F. |
| 122°F..... | | | | | | | | | | | | |
| 140..... | 2.5 | 1.5 | 1 | 1.0 | .5 | 1.0 | .5 | .5 | .5 | | | |
| 158..... | | | | 3.5 | 2.5 | 3.0 | 2.0 | 2.0 | 2.5 | | | |
| 176..... | 7.0 | 6.0 | 5.5 | 6.5 | 5.0 | 5.5 | 5.0 | 4.5 | 5.0 | | | |
| 194..... | 10.0 | 9.0 | 9.5 | 9.5 | 9.0 | 9.5 | 8.5 | 7.5 | 9.0 | | | |
| 212..... | 13.5 | 12.0 | 13.0 | 16.0 | 14.0 | 14.5 | 13.5 | 12.0 | 14.0 | | | |
| 230..... | 18.0 | 16.5 | 17.5 | 21.5 | 21.0 | 21.5 | 20.0 | 18.5 | 20.0 | | | |
| 248..... | 23.0 | 21.5 | 23.5 | 31.5 | 30.0 | 30.5 | 29.0 | 26.5 | 28.5 | | | |
| 266..... | 29.0 | 27.5 | 29.0 | 42.0 | 40.0 | 40.5 | 38.0 | 36.0 | 39.0 | | | |

| | Naphtha | | | Gasolines | | | | | | Bottoms | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 6 Lbs. 2½–1 | | | 70 % Cut | | | 74 % Cut | | | Crude | Acid | Gel |
| | Crude | Acid | Gel | Crude | Acid | Gel | Crude | Acid | Gel | | | |
| DISTILLATIONS: | | | | | | | | | | | | |
| 284 | 36.5 | 34.0 | 36.0 | 50.0 | 50.5 | 52.0 | 47.0 | 46.5 | 49.5 | | | |
| 302 | 43.0 | 41.0 | 42.5 | 61.0 | 61.0 | 63.0 | 58.0 | 57.5 | 59.5 | | | |
| 320 | 48.5 | 47.5 | 49.0 | 72.5 | 71.0 | 73.5 | 68.5 | 67.5 | 69.5 | | | |
| 338 | 54.5 | 54.0 | 55.0 | 81.5 | 79.0 | 82.0 | 76.0 | 76.5 | 78.0 | | | |
| 356 | 61.0 | 60.0 | 62.0 | 88.0 | 86.0 | 88.0 | 84.5 | 83.5 | 85.5 | | | |
| 374 | 66.0 | 65.5 | 67.0 | 92.0 | 91.0 | 92.5 | 89.5 | 89.0 | 90.5 | | | |
| 392 | 71.0 | 71.0 | 73.0 | 94.5 | 94.0 | 95.0 | 93.0 | 92.5 | 93.5 | | | |
| 410 | 76.5 | 76.0 | 77.5 | 96.0 | 96.0 | 96.5 | 95.0 | 95.0 | 95.5 | | | |
| 428 | 80.0 | 80.0 | 81.5 | 97.0 | 97.0 | | 96.0 | 96.5 | 97.0 | 2.0 | 3.5 | 4.0 |
| 446 | 84.0 | 84.0 | 85.0 | | | | | | | 16.5 | 22.5 | 21.0 |
| 464 | 87.0 | 86.5 | 88.5 | | | | | | | 40.0 | 45.0 | 44.5 |
| 482 | 90.0 | 90.0 | 91.0 | | | | | | | 59.0 | 60.0 | 61.5 |
| 500 | 92.0 | 92.0 | 93.0 | | | | | | | 71.5 | 71.0 | 72.0 |
| 518 | 93.5 | 94.0 | 95.0 | | | | | | | 80.0 | 79.5 | 81.0 |
| 536 | 94.5 | 95.0 | 96.0 | | | | | | | 86.5 | 86.0 | 86.5 |
| 554 | 95.5 | 96.0 | | | | | | | | 93.0 | 89.5 | 91.0 |
| 572 | | | | | | | | | | 94.5 | 92.5 | 92.5 |
| 590 | | | | | | | | | | 95.5 | 94.0 | 94.0 |
| 608 | | | | | | | | | | 96.5 | 95.5 | 97.0 |
| Drain | 96.5 | 97.0 | 97.5 | 97.5 | 97.5 | 95.7 | 97.5 | 97.5 | 97.5 | 98.0 | 97.5 | 98.0 |
| End Point | 556°F. | 566°F. | 551°F. | 431°F. | 437°F. | 419°F. | 445°F. | 450°F. | 435°F. | 615°F. | 623°F. | 611°F. |

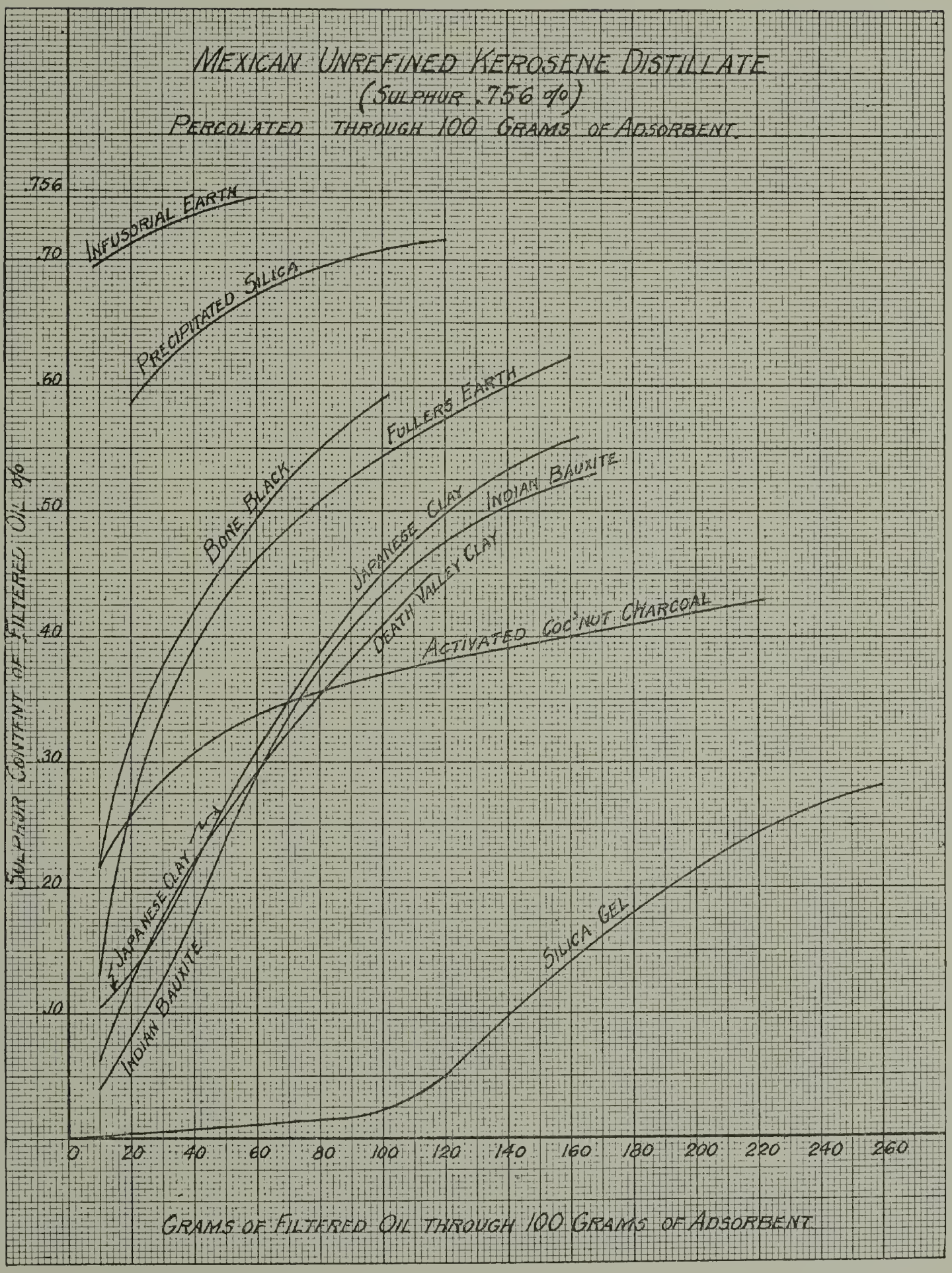

MEXICAN UNREFINED KEROSENE DISTILLATE
(SULPHUR .756 %)
PERCOLATED THROUGH 100 GRAMS OF ADSORBENT
SULPHUR CONTENT OF FILTERED OIL %
.756
.70
.60
.50
40
30
20
10
INFUSORIAL EARTH
PRECIPITATED SILICA
BONE BLACK
FULLER'S EARTH
JAPANESE CLAY
INDIAN BAUXITE
DEATH VALLEY CLAY
ACTIVATED COC'NUT CHARCOAL
JAPANESE CLAY
INDIAN BAUXITE
SILICA GEL
0 20 40 60 80 100 120 140 160 180 200 220 240 260
GRAMS OF FILTERED OIL THROUGH 100 GRAMS OF ADSORBENT
5-21-23

PLATE NO. 14

point, and a very definite method of determining accurately this end point has been set forth in the government bulletins. Our reference hereafter to "Gasoline" will always be, therefore, to the fraction above mentioned as "New Navy" motor gasoline.

The present study was made on a naphtha distillate which is a representative sample of the average naphtha being refined by one of the largest Atlantic Seaboard refineries. It contained both straight run and cracked distillates, and was made from a combination of all crude oils now commonly used by Seaboard refineries. It may therefore be considered quite representative of the bulk of gasoline produced by Eastern refineries.

The yield of gasoline obtained from a given quantity of naphtha distillate when refined by present methods, is diminished in two distinct ways. First, by actual shrinkage of volume; and second, by raising the boiling point of certain unsaturated hydrocarbons, through polymerization of these unsaturated bodies. Such polymerization is brought about by reaction between the sulphuric acid used for refining the distillate, and the above mentioned unsaturated hydrocarbons; the effect being to produce higher boiling fractions out of a portion of the gasoline present, and to this extent reducing the gasoline content of the naphtha being refined.

In the case of gel treatment of the crude naphtha, there is no polymerization effect whatsoever, because of the purely physical nature of the treatment. There is, on the other hand, an actual increase in the gasoline yield due to the selective removal of the high-boiling sulphur compounds; the net result being an increased yield by gel treatment amounting to 4 per cent of the original distillate. This 4 per cent difference is a combination of the two above mentioned effects, namely, the loss of gasoline when treated chemically, due to polymerization of unsaturated bodies, and the increased yield when gel treated, due to removal of high boiling sulphur compounds.

The shrinkage in volume, due to chemical treatment, will vary somewhat with the amount of acid used for treatment, and is more difficult to determine accurately on a small scale than is the gasoline content of the refined naphtha above mentioned. From information obtained from various refiners treating this kind of naphtha, we believe this loss to be not less than 2.0 per cent.

The total loss of gasoline present in the original unrefined distillate is, therefore, as follows:

| | |
|---|---|
| Loss by volume shrinkage | 2.00% |
| Reduction of gasoline yield by polymerization | 4.00% |
| Total | 6.00% |

The loss due to shrinkage of volume is well known to all refiners, and has been the only loss that heretofore has claimed their attention. This position may have been a sound one to take before the advent of cracked gasoline, but now that every refiner is face to face with the absolute certainty of handling a mixture of straight run and cracked distillates, he has also to deal with the loss by polymerization above referred to. And since this loss is about twice that due to volume shrinkage alone, it is a correspondingly greater menace to his final yield of gasoline.

The curves and tabulations, Plates Nos. 15, 16 and 17, show the yields of New Navy gasoline from naphtha refined by the silica gel process, as compared to the yield from the same original naphtha refined by the ordinary chemical treatment with sulphuric acid. It is hardly necessary to give a detailed description of these charts, except to call attention to the fact that a distinctly superior grade of gasoline was obtained by the gel treatment in addition to the increased yield secured.

## Costs of Refining Average Grade Gasoline Produced by Atlantic Seaboard Refineries

### *Chemical Treatment Versus Silica Gel*

*Assumptions:*

*Naphtha* containing 65 per cent Gasoline treated by chemical method, with subsequent fire and steam distillation.

*Gasoline distillate* cut to proper end point on primary stills, refined with silica gel.

Refining Costs per Barrel of Distillate

| | Chemical Treatment | Silica Gel |
|---|---|---|
| Sulphuric Acid | $ .055 | |
| Caustic and Litharge | .027 | |
| Labor | .008 | $ .006 |
| Power | .010 | .013 |
| Repairs | .008 | .005 |
| Fuel | .... | .015 |
| Steam | ..... | .006 |
| Distillation (Fire and Steam) | .080 | |

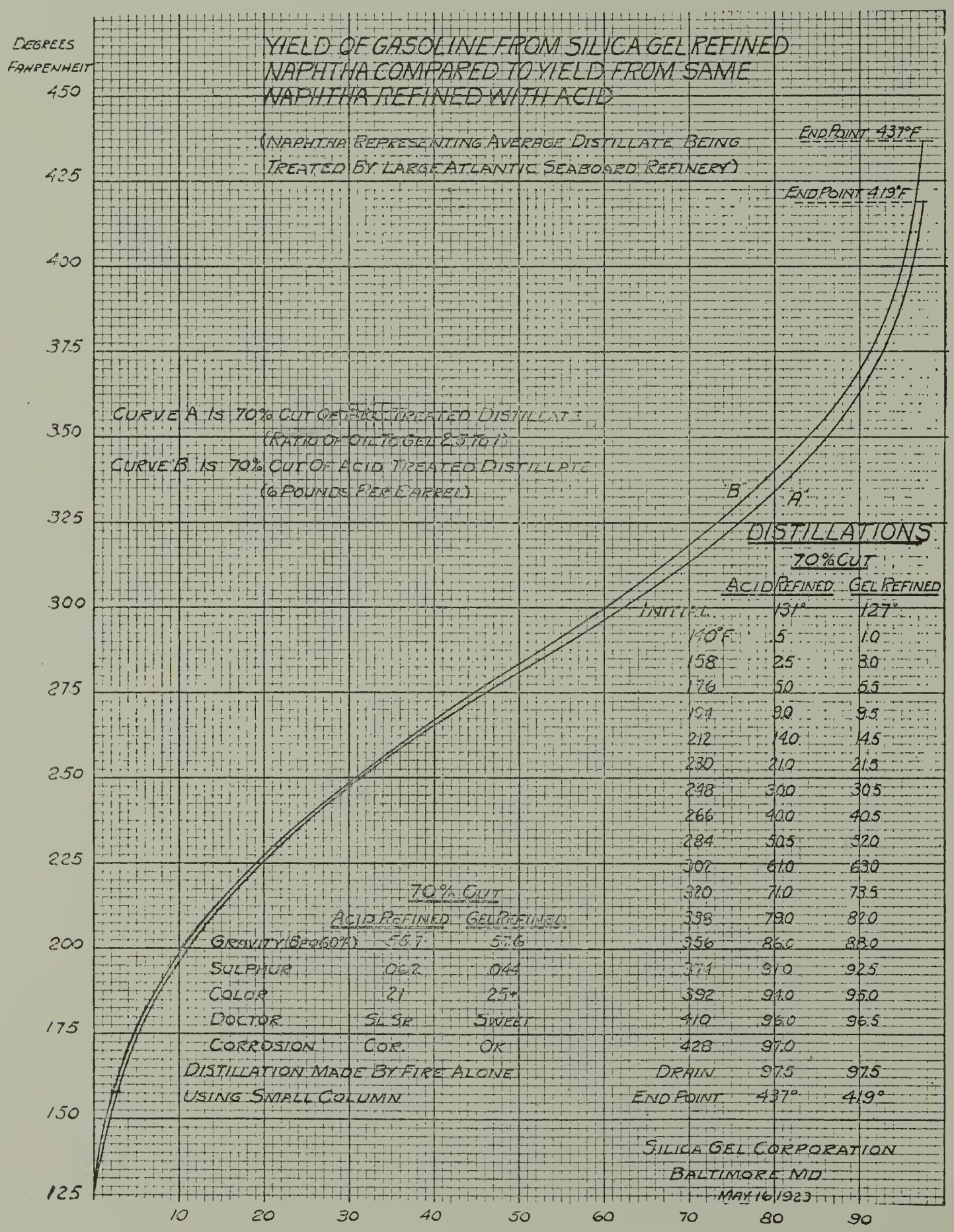

DEGREES FAHRENHEIT
450
425
400
375
350
325
300
275
250
225
200
175
150
125
YIELD OF GASOLINE FROM SILICA GEL REFINED NAPHTHA COMPARED TO YIELD FROM SAME NAPHTHA REFINED WITH ACID
(NAPHTHA REPRESENTING AVERAGE DISTILLATE BEING TREATED BY LARGE ATLANTIC SEABOARD REFINERY)
END POINT 431°F
END POINT 419°F
CURVE A IS 70% CUT OF GEL TREATED DISTILLATE
(RATIO OF OIL TO GEL 5 TO 1)
CURVE B IS 70% CUT OF ACID TREATED DISTILLATE
(6 POUNDS PER BARREL)
B
A
DISTILLATIONS
70% CUT
ACID REFINED
GEL REFINED
INITIAL 131° 127°
140°F .5 1.0
158 2.5 3.0
176 5.0 5.5
194 9.0 9.5
212 14.0 14.5
230 21.0 21.5
248 30.0 30.5
266 40.0 40.5
284 50.5 52.0
302 61.0 63.0
320 71.0 73.5
338 79.0 82.0
356 86.0 88.0
374 91.0 92.5
392 94.0 95.0
410 96.0 96.5
428 97.0
DRAIN 97.5 97.5
END POINT 437° 419°
70% CUT
ACID REFINED
GEL REFINED
GRAVITY (BE@60°F) 56.7 57.6
SULPHUR 0.12 0.11
COLOR 21 25+
DOCTOR SL SR SWEET
CORROSION COR. OK
DISTILLATION MADE BY FIRE ALONE
USING SMALL COLUMN
SILICA GEL CORPORATION
BALTIMORE MD
MAY 16 1923
10
20
30
40
50
60
70
80
90
PERCENT DISTILLED OVER

PLATE NO. 15

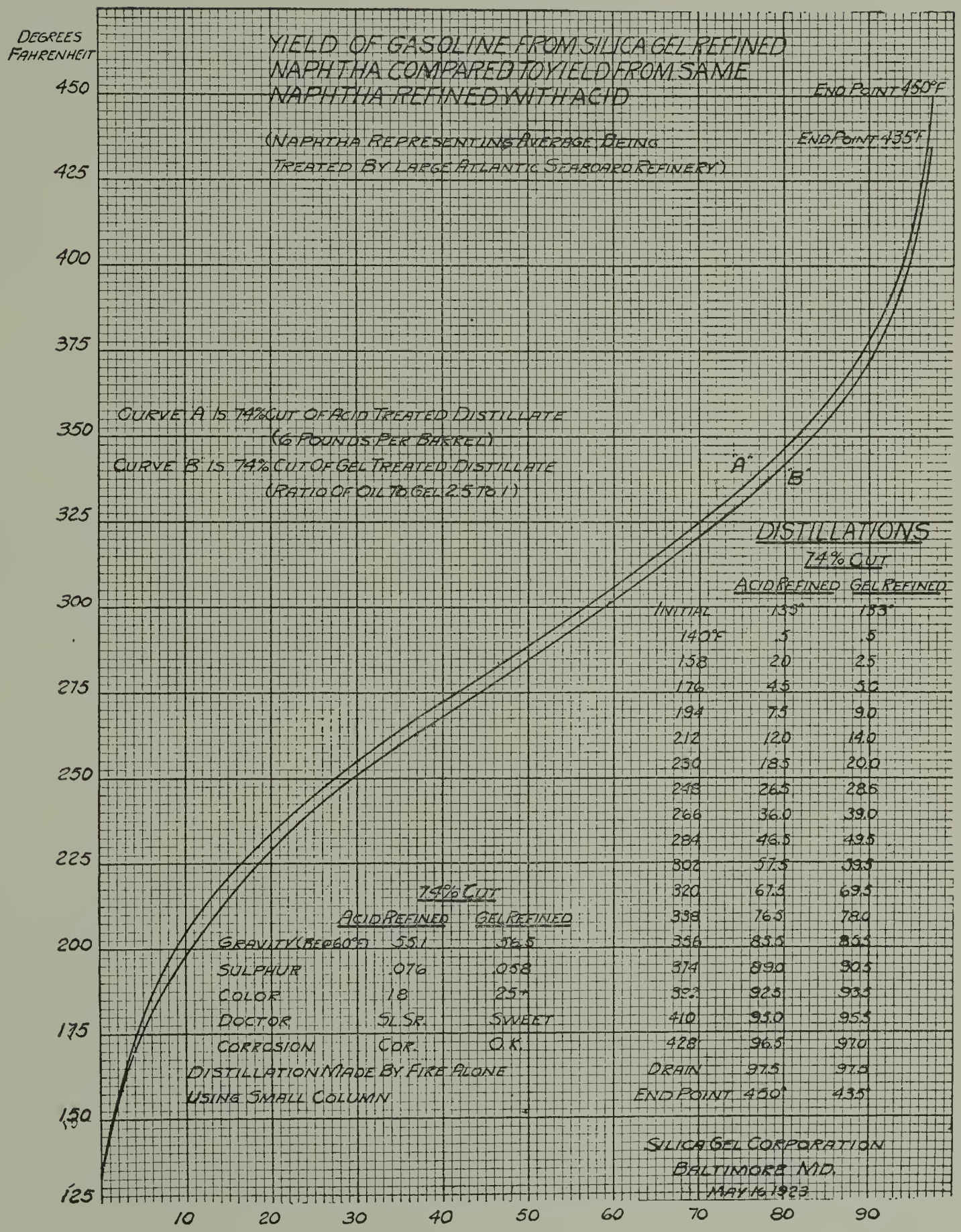

DEGREES FAHRENHEIT
YIELD OF GASOLINE FROM SILICA GEL REFINED NAPHTHA COMPARED TO YIELD FROM SAME NAPHTHA REFINED WITH ACID
(NAPHTHA REPRESENTING AVERAGE BEING TREATED BY LARGE ATLANTIC SEABOARD REFINERY)
END POINT 450°F
END POINT 435°F
CURVE A IS 74% CUT OF ACID TREATED DISTILLATE (6 POUNDS PER BARREL)
CURVE B IS 74% CUT OF GEL TREATED DISTILLATE (RATIO OF OIL TO GEL 2.5 TO 1)
A'
B'
450
425
400
375
350
325
300
275
250
225
200
175
150
125
10
20
30
40
50
60
70
80
90
PERCENT DISTILLED OVER
DISTILLATIONS
74% CUT
ACID REFINED GEL REFINED
INITIAL 153° 153°
140°F .5 .5
158 2.0 2.5
176 4.5 5.0
194 7.5 9.0
212 12.0 14.0
230 18.5 20.0
248 26.5 28.6
266 36.0 39.0
284 46.5 49.5
302 57.5 59.5
320 67.5 69.5
338 76.5 78.0
356 83.5 85.5
374 89.0 90.5
392 92.5 93.5
410 95.0 95.5
428° 96.5 97.0
DRAIN 97.5 97.8
END POINT 450° 435°
74% CUT
ACID REFINED GEL REFINED
GRAVITY (BE@60°F) 55.1 56.5
SULPHUR .076 .058
COLOR 18 25+
DOCTOR SL. SR. SWEET
CORROSION COR. O.K.
DISTILLATION MADE BY FIRE ALONE USING SMALL COLUMN
SILICA GEL CORPORATION
BALTIMORE MD.
MAY 16 1923

PLATE NO. 16

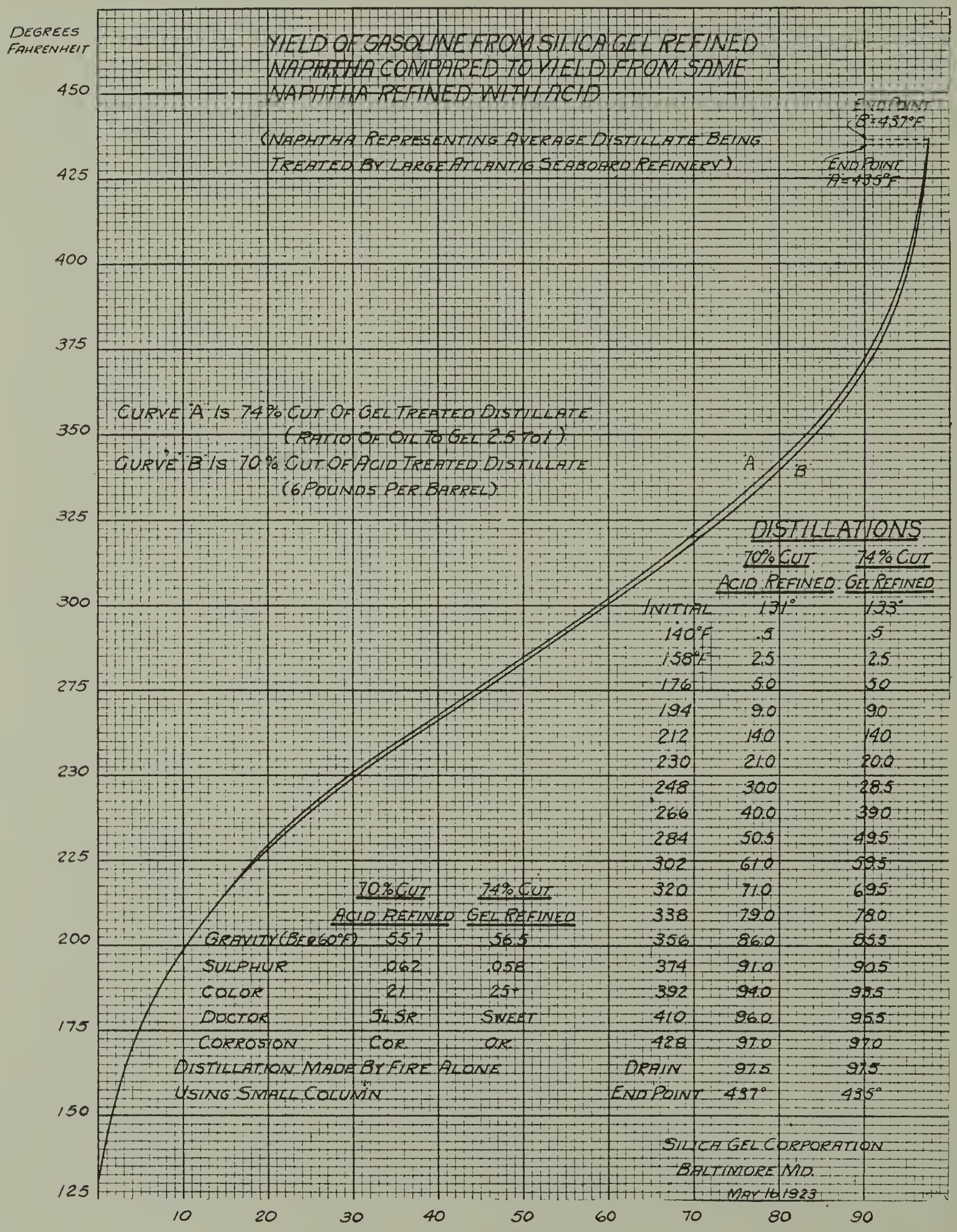

DEGREES FAHRENHEIT
YIELD OF GASOLINE FROM SILICA GEL REFINED NAPHTHA COMPARED TO YIELD FROM SAME NAPHTHA REFINED WITH ACID
(NAPHTHA REPRESENTING AVERAGE DISTILLATE BEING TREATED BY LARGE ATLANTIC SEABOARD REFINERY)
END POINT B=437°F
END POINT A=435°F
CURVE 'A' IS 74% CUT OF GEL TREATED DISTILLATE (RATIO OF OIL TO GEL 2.5 TO 1)
CURVE 'B' IS 70% CUT OF ACID TREATED DISTILLATE (6 POUNDS PER BARREL)
A
B
DISTILLATIONS
70% CUT ACID REFINED
74% CUT GEL REFINED
INITIAL 131° 133°
140°F .5 .5
158°F 2.5 2.5
176 5.0 5.0
194 9.0 9.0
212 14.0 14.0
230 21.0 20.0
248 30.0 28.5
266 40.0 39.0
284 50.5 49.5
302 61.0 59.5
320 71.0 69.5
338 79.0 78.0
356 86.0 85.5
374 91.0 90.5
392 94.0 93.5
410 96.0 95.5
428 97.0 97.0
DRAIN 97.5 97.5
END POINT 437° 435°
70% CUT ACID REFINED
74% CUT GEL REFINED
GRAVITY (BE @ 60°F) 55.7 56.5
SULPHUR .062 .058
COLOR 21 25+
DOCTOR SL. SR. SWEET
CORROSION COR. O.K.
DISTILLATION MADE BY FIRE ALONE USING SMALL COLUMN
SILICA GEL CORPORATION BALTIMORE MD. MAY 16 1923
450
425
400
375
350
325
300
275
250
225
200
175
150
125
10
20
30
40
50
60
70
80
90
PERCENT DISTILLED OVER

PLATE NO. 17

| | | |
|---|---|---|
| Total Operating Cost per Barrel of Distillate Treated | $ .188 | $ .045 |
| TREATMENT LOSS @ $ .15 PER GALLON GASOLINE: | | |
| Chemical Method 2% | .126 | |
| Silica Gel .75% | | .047 |
| LOSS OF GASOLINE YIELD DUE TO POLYMERIZATION: | | |
| (Charged at difference of value between Gasoline and Naphtha Bottoms.) | | |
| For Chemical Treatment 3% @ $ .10 per Gallon | .120 | |
| DEPRECIATED VALUE OF GASOLINE IN RECOVERED OIL: | | |
| Silica Gel Method 1.00 % @ $ .12 per Gallon | | .051 |
| SILICA GEL REPLACEMENT AND ROYALTY AT $ .001 PER POUND OF GEL USED | | .076 |
| Total Refining Cost per Barrel of Distillate | $ .434 | $ .219 |
| Total Refining Cost per Barrel of *Gasoline* at 65% Gasoline in Refined Naphtha | .667 | |
| Total Refining Cost by Silica Gel | .219 | |
| Saving per Barrel of Gasoline | $ .448 | |

## REFINING COSTS BY SILICA GEL PROCESS COMPARED TO PRESENT METHODS

The only unfriendly criticism the gel process of refining has had is based on a misunderstanding on the part of some as to the cost of this treatment. That a superior product is obtained is acknowledged by all who have seriously investigated the process. The average refiner has argued, however, that he could charge no more for better products, and is therefore unwilling to make any change that would increase his present costs, even though by so doing he could furnish superior products. While we do not agree with his conclusion, it in no way embarrasses the silica gel refining process, since we have conclusively shown by operation on a commercial scale that a very large reduction in the total cost of refining is effected, concurrently with the better refining above mentioned.

The tabulation of comparative costs, shown above, is based on the assumption that in the case of gel treatment a gasoline distillate of proper end-point will be cut directly on the primary stills. This avoids the re-run distillation now customarily made after a chemical treatment, and furthermore reduces the quantity of distillate to be treated, by approximately 35 per cent.

The chief advantages of the gel process, which results in less refining costs, may be briefly stated as follows:

1. Reduced quantity of distillate to be refined.
2. Elimination of re-run distillation.
3. Increased yield of gasoline.

We believe, therefore, that the silica gel process will earn the reputation of greater yield of better gasoline at lower costs.

# THE CAPILLARY THEORY OF ADSORPTION FROM SOLUTION

By W. A. PATRICK

Read at the Wilmington, Del., Meeting, June 20, 1923

The following paper is an attempt to apply the theory of capillarity to the adsorption of dissolved substances from solution. Needless to say, capillarity is not considered to be the only mechanism of adsorption, but it is to be regarded as an important factor in all phases of adsorption. In fact it is doubtful if the effect of capillarity is ever absent except in observations carried out at temperatures considerably above the critical temperature of the adsorbed substance. In this connection it is well to remember that no measurements have ever been made with a plane surface as the adsorbent.

For the sake of clearness a short sketch of the capillarity theory as applied to the adsorption of vapors will be given. The fundamental relationships of capillarity may be concisely expressed by the following formula:

$$ln \frac{p}{p_0} = -\frac{2\sigma M}{RT\delta r}$$

which gives the vapor pressure ($p$) of a concave surface of liquid of radius of curvature ($r$), surface tension ($\sigma$), molecular weight ($M$), density ($\delta$), and vapor pressure ($p_0$), at temperature ($T$). It may be said that the above relationship gives a correct qualitative description of the phenomenon of the condensation of a vapor to a liquid in a capillary tube. Applying these ideas to the phenomenon of adsorption by porous bodies, it is seen that a greater reduction of vapor pressure is produced in small tubes than in arge ones and, furthermore, it is apparent that the higher the surface tension of a liquid the more easy it is to condense the corresponding vapor. The difficulty is encountered that pores of molecular dimension must be assumed in order to account for the lowering of vapor pressure produced. It will be the purpose of this paper to show how this objection may be met and also what

modifications are necessary when dealing with the adsorption of dissolved substances from solution.

The adsorption of the following gases by silica gel has been measured at various pressures and temperatures; sulphur dioxide, carbon dioxide, ammonia, and butane. It is to be noted that these four gases present wide differences in chemical and physical properties. The results obtained may best be shown graphically (Fig. 1).

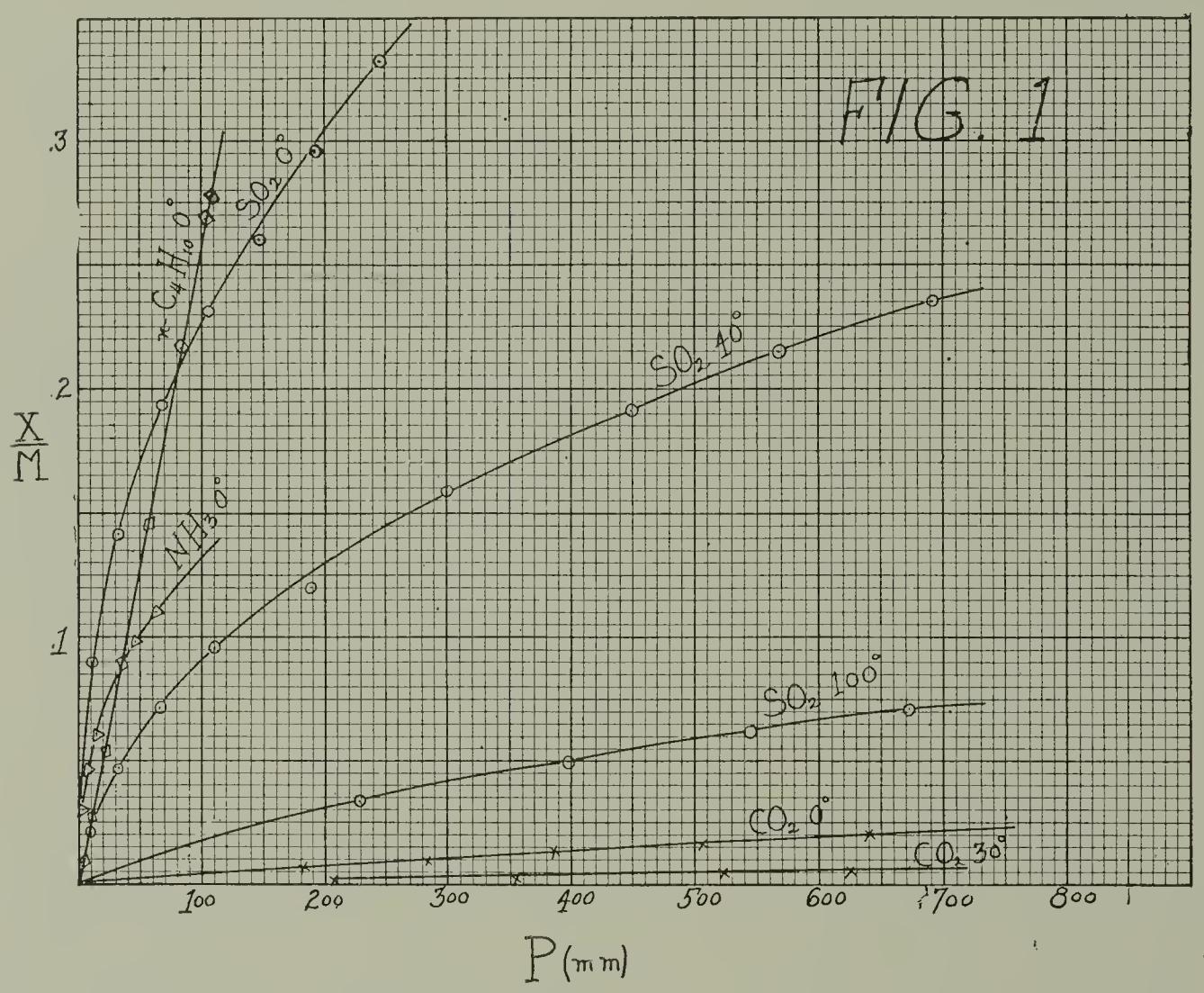



FIG. 1.

These results are sufficient to show the diversity of the facts to be correlated. Considering adsorption as the filling of the capillary pores of the adsorbent, it is apparent that one must not express the extent of adsorption in terms of mass, but rather as the volume of the liquid. Furthermore it is not to be expected that condensation of different vapors will occur at the same pressure. Taking the basic formula of capillarity as our guide let us now express our experimental results in the following graphical manner (Fig. 2). Fig. 3 is the corresponding log. curve.

It will be seen that practically all the points of the curves of

Fig. 1 are represented by a single curve. From this fact a number of important conclusions may be drawn. In the first place the equation of the curve of Fig. 2 may be written down and it will enable

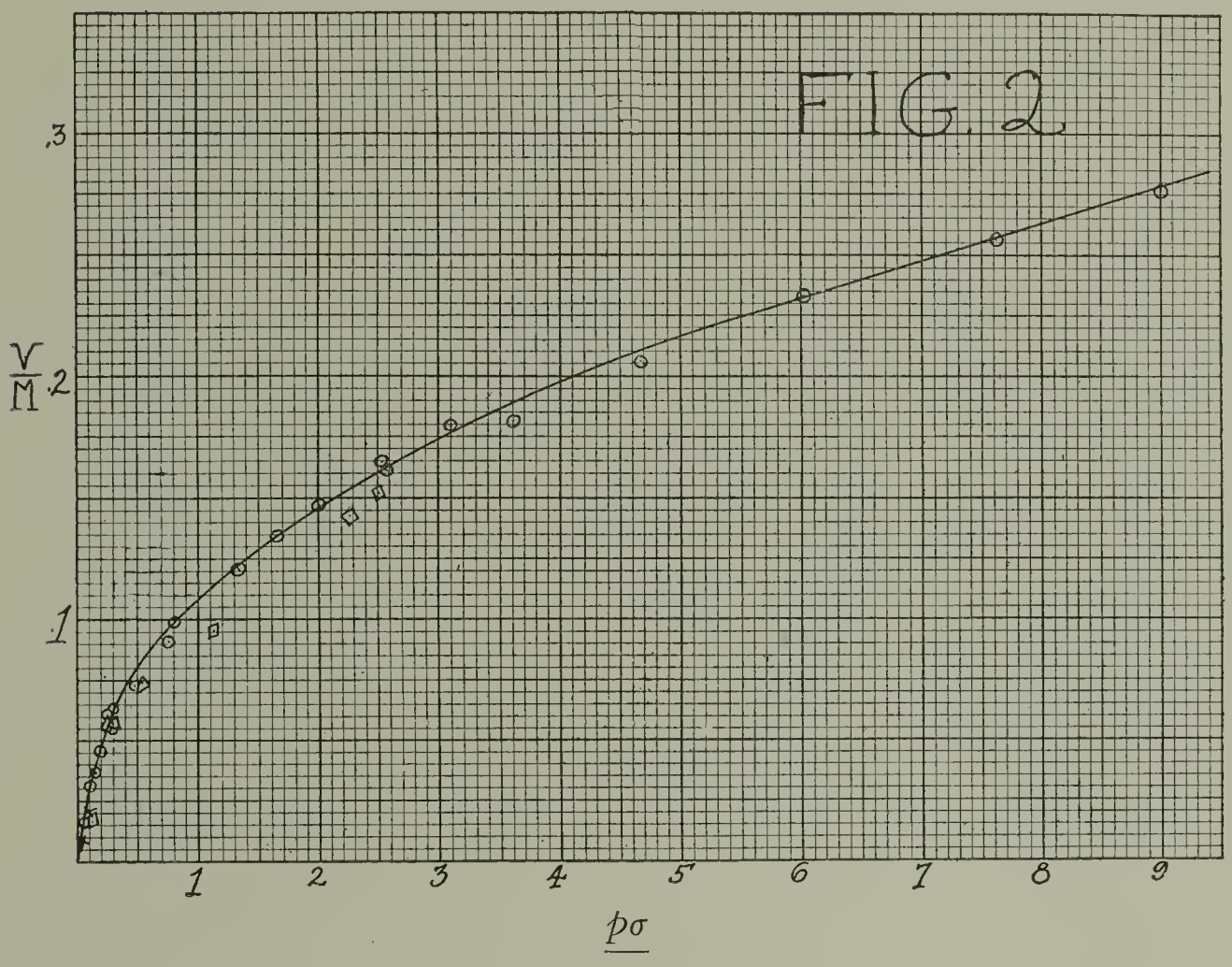



Fig. 2.

one to express the extent of the adsorption of any of the four gases at any temperature or pressure. This is a practical result of considerable value. The equation takes the form

$$V = K\left(\frac{p\sigma}{p_0}\right)^{1/n}$$

While the equation, as is evident by inspection of Fig. 2, is capable of very closely representing the course of the adsorption it must nevertheless be regarded as an approximation. This fact is evident from both practical and theoretical considerations. In other words, capillary forces are not the only means by which silica gel retains gases, and from the theoretical side it can be shown that the above formula cannot be deduced from the basic thermodynamic principle of capillarity. The above expression must therefore be regarded

as a purely empirical relationship. Notwithstanding the limitations of the above formula it enables us to gain considerable insight into the workings of the forces of capillarity, and in addition it enables us to say with considerable certainty that the main factors that determine the extent of adsorption of a gas are the physical properties of the liquid resulting from the condensation of the gas, i.e., density, surface tension, vapor pressure, molecular weight. Furthermore the above formula enables us to draw the very important

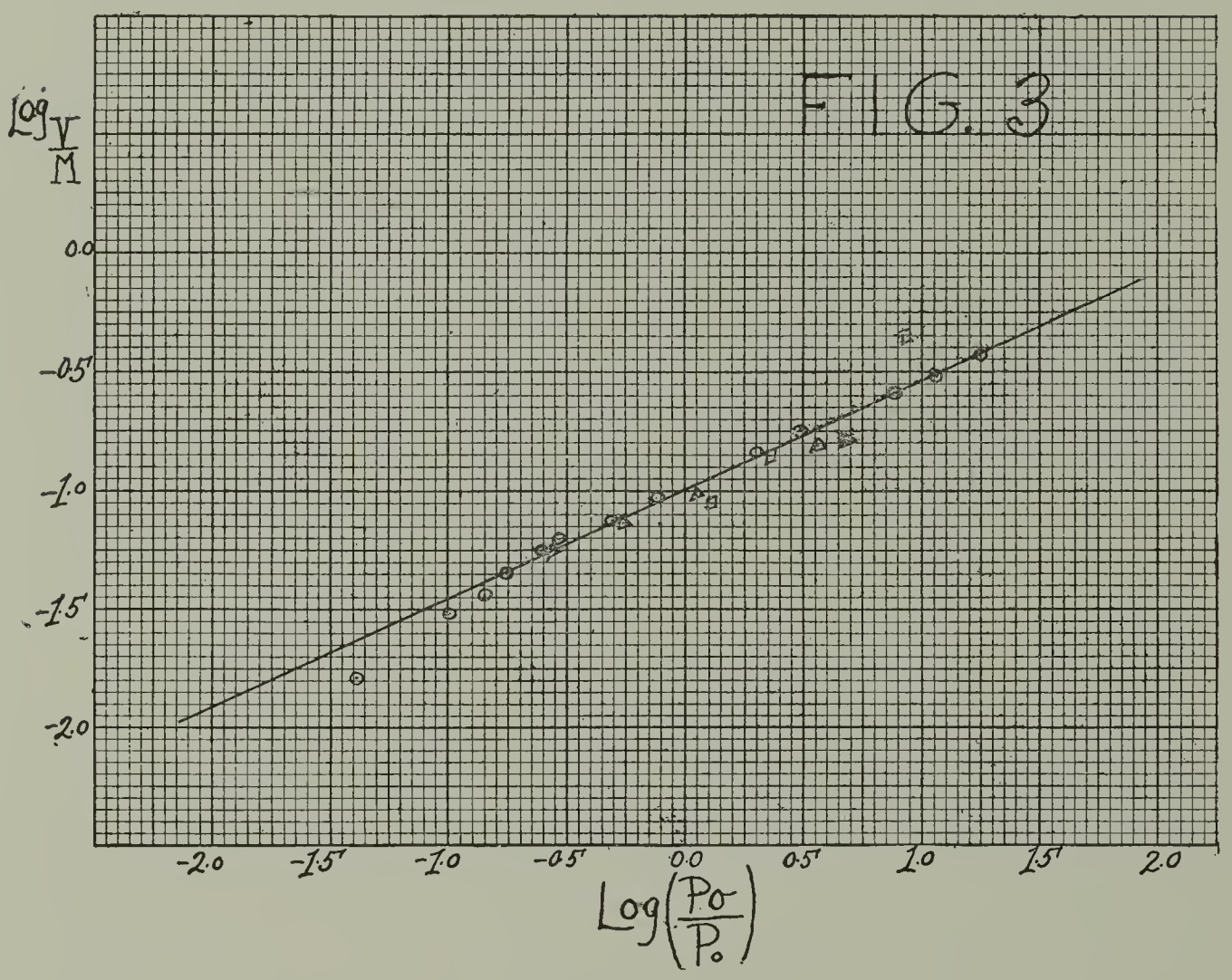



FIG. 3.

conclusion that the surface tension of a liquid exhibiting capillarity curvature is not constant but changes with the radius of curvature. This fact is evident from the form of the empirical adsorption equation where it is seen that the surface tension is raised to a fractional power, which makes the surface tension greater in the initial stages of the adsorption than in the latter stages. This variation of the surface tension with the radius of curvature is one of the most important results of this work and is an idea that will require considerable elucidation and much more supporting evidence before

it can be firmly established. It is our firm belief, however, that further research will fully vindicate our present position. For the present we will start with this assumption and indicate its effect on the phenomena of adsorption as exhibited by porous bodies.

It is possible to derive an adsorption formula from the basic relationship of capillarity

$$ln\frac{p}{p_0} = -\frac{2\sigma M}{RT\delta r} \tag{1}$$

by combining it with the equation

$$V = Kr^{1/n} \tag{2}$$

which simply expresses the fact that our adsorbent is a porous body made up of pore spaces of various sizes.

By differentiating both of these equations with respect to $r$ we may eliminate the latter and obtain a relation between $V$ and $p/p_0$ which is nothing more than an equation of adsorption.

$$dV = K_n/r^{1/n-1}dr$$

$$dr = -\frac{\delta RTr^2 d(lnp_0/p)}{2\sigma M}$$

eliminating $dr$ we obtain

$$d(lnp_0/p) = -\frac{2K^n n\sigma M}{\delta RT}\frac{dV}{V^{n\mp 1}}$$

integrating

$$V^{-n} = \frac{lnp_0/p}{\frac{2K^n\sigma M^7}{\delta RT}} - C$$

when $p = p_0$ the adsorbent is saturated and the volume is then equal to the total internal volume of the gel ($V_0$). Therefore $C = V_0{}^{-n}$ and

$$1/V^n - 1/V_0{}^n = \frac{\delta RT}{nR^n\sigma M} ln(p_0/p) \tag{3}$$

Here we have an adsorption relationship that is rigorously derived from only two assumptions namely: that capillary forces are responsible for the adsorptive power, and secondly that the adsorbent contains capillaries of various sizes.

This formula may be tested as follows: By means of equation (1) values of $r$ may be calculated corresponding to various values of $(p/p_0)$. Equation (1) may be cast in the following form when $r$ is expressed in $\mu\mu$.

$$r = \frac{2\sigma M 10^7(.4343)}{\delta(8.3 \times 10^7)T \log p/p_0}$$

Substitution of these values of $r$ in equation (2) will enable one to ascertain whether $K$ and $1/n$ are constants.

Table (1) represents a typical calculation, namely that of the

TABLE I

| $\log \frac{P}{P_0}$ | $\log V$ | Temp. | $r(\mu\mu)$ | $\frac{1}{n}$ | $K \times 10^{-6}$ |
|---|---|---|---|---|---|
| $\bar{1}.06711$<br>$\bar{1}.22883$ | $\bar{1}.21380$<br>$\bar{1}.28652$ | 30° (near saturation) | 0.41<br>— | .879<br>— | .644<br>— |
| $\bar{1}.16702$<br>$\bar{1}.08077$ | $\bar{1}.25355$<br>$\bar{1}.21436$ | 40° (near saturation) | 0.41<br>— | .916<br>— | .724<br>— |
| $\bar{2}.50189$<br>$\bar{2}.41060$ | $\bar{2}.80302$<br>$\bar{2}.75343$ | 100° (near saturation) | 0.10<br>— | 1.930<br>— | 18.545<br>— |
| $\bar{2}.06453$<br>$\bar{3}.33415$ | $\bar{2}.73466$<br>$\bar{2}.39811$ | 30° (far from saturation) | 0.19<br>— | 2.420<br>— | 13.806<br>— |
| $\bar{1}.70435$<br>$\bar{1}.49337$ | $\bar{1}.57984$<br>$\bar{1}.49483$ | −54° (near saturation) | 2.57<br>— | 0.363<br>— | 0.339<br>— |

adsorption results obtained by studying the system silica gel—sulphur dioxide at various pressures and temperatures. It is to be noted that $K$ and $1/n$ are not constant. Furthermore it is to be observed that the radii of the capillary spaces are of molecular dimension. In some cases it is even necessary to assume spaces that are less than .2 $\mu\mu$ in diameter. These facts show that our formula (3) cannot be regarded as a workable one notwithstanding the fact that it is rigorously derived from assumptions that are apparently sound.

Our difficulties are more easily overcome by the assumption that equation (1) does not correctly represent the influence of capillarity in the very fine pores. In other words we must not look upon the surface tension of a liquid as being independent of the radius of curvature, but must regard it as being greater in the case

of highly concave surfaces and smaller in the case of highly convex surfaces i.e. small drops. This assumption is sufficient to correlate all of our adsorption results in a rational manner, but unfortunately we are not able to give quantitative expression to this view. Consequently we must have recourse to our empirical formula as a means of concisely presenting our experimental results.

Applying the above ideas to the adsorption of dissolved substances from solution it is obvious that certain changes must be made. Instead of the vapor pressure being affected by the energy of the surface we have the analogous effect upon the solute. In other words, we assume that a solute of highly curved concave surface will exhibit a lower solubility than that of a plane surface. Furthermore instead of surface tension we must utilize the interfacial tension between the phase in the capillaries and the exterior phase. Pursuing these ideas it follows that that component of a solution will be adsorbed by a porous adsorbent that most easily wets the same, or in other words that exhibits the smallest surface tension toward the adsorbent. If we make the further assumption that the walls of our capillary spaces are essentially that of a water surface, as they are in most of our silica gels, then we are in a position to predict what component of a given solution will be adsorbed by silica gel. This prediction requires only a knowledge of the interfacial tensions between water and the components of the solution.

These views have been tested by measuring the adsorption produced with silica gel from a great number of solutions, namely: formic acid in nitrobenzene and toluene; acetic acid in nitrobenzene, toluene, carbon tetrachloride, carbon disulphide, and kerosene; n-butyl alcohol in benzene; n-butyric acid in toluene, kerosene, and gasoline. In all of these solutions the results of our predictions as to which component would be adsorbed by the gel was in every case verified by the experiment.

As far as the quantitative aspect of the problem is concerned our ideas may best be represented by means of our experimental results obtained by the study of the system n-butyl alcohol-water. We very carefully measured the adsorption of water from solutions of water in n-butyl alcohol. The results are most easily seen in Fig. 4, where the volume of water adsorbed is plotted as ordinates against the concentration ($S$) of water in the butyl alcohol when the system (gel + solution) has reached equilibrium.

The results may best be discussed by means of the empirical formula. (See Fig. 5.)

$$V = K\left(\frac{S\sigma}{S_0}\right)^{1/n}$$

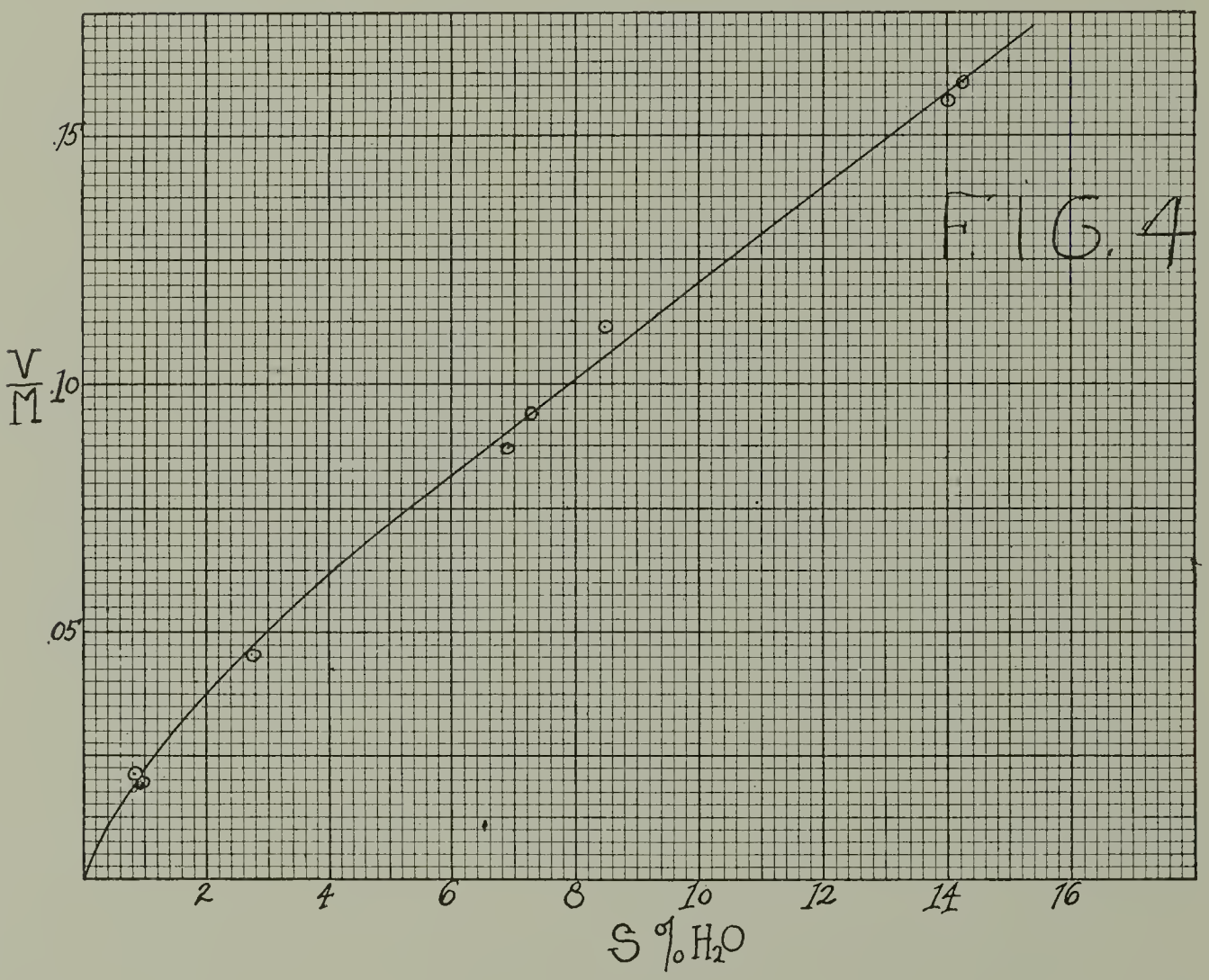



FIG. 4.

where ($S$) represents the equilibrium concentration of the water in butyl alcohol and ($S_0$) the "solubility" of a plane surface of water in butyl alcohol. Putting the equation in the logarithmic form, we have

$$\log V = 1/n \log (S\sigma) + \log K - 1/n \log (S_0)$$

by plotting $V$ against $\log (S\sigma)$ a straight line should be obtained with the slope of $1/n$ and an intercept on the $\log V$ axis of

$$\log K - 1/n \log S_0$$

At 25° C. our measurements when cast in this form gave a value of

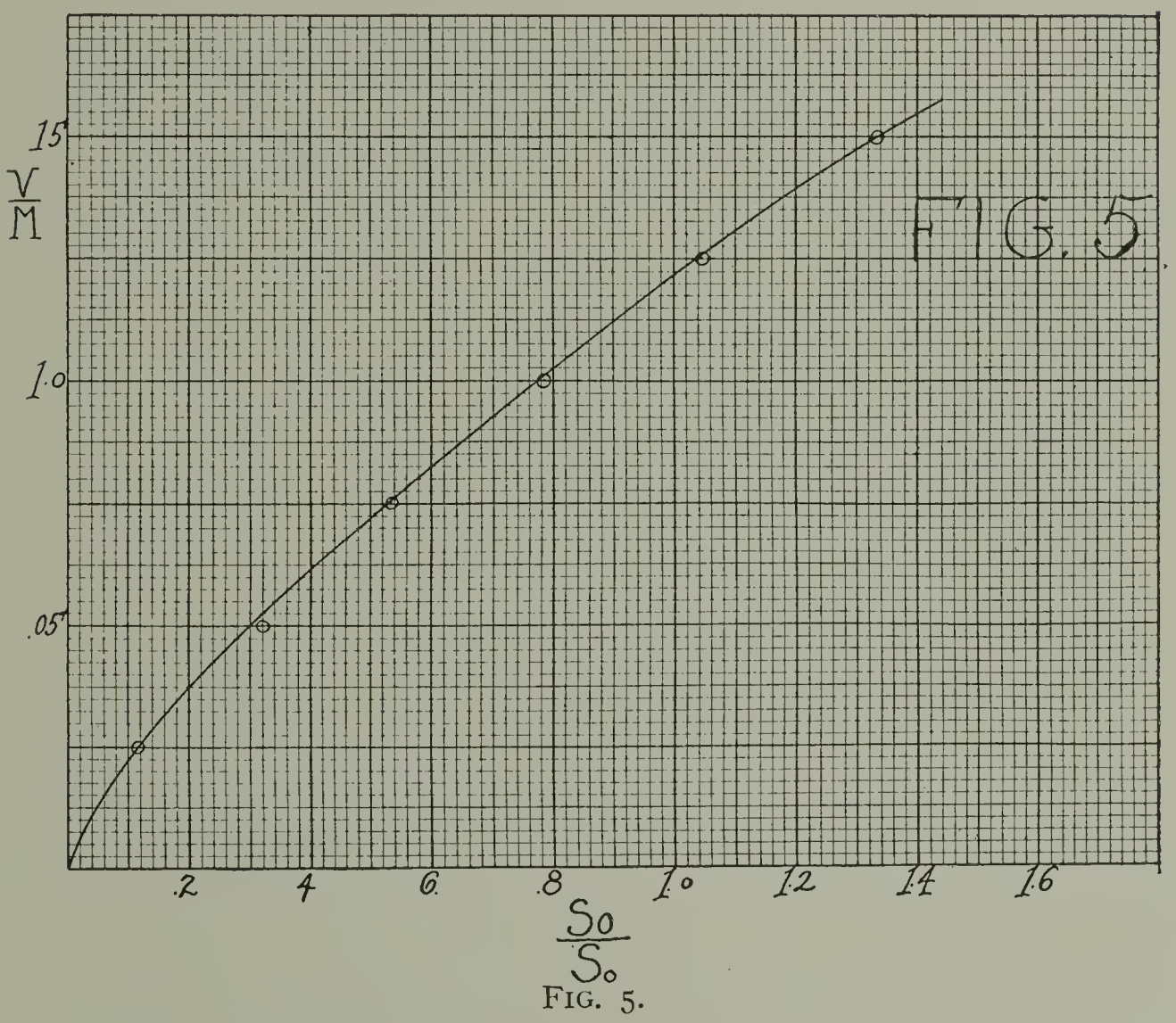
$$1/n = .767$$

When $S = S_0$, i.e., at saturation

$$V_0 = K\sigma^{1/n} \qquad \text{or} \qquad K = \frac{V_0}{\sigma^{1/n}}$$

The volume of water taken up by the gel was found to be 0.2 c.c. per gram at saturation. Therefore $K = \frac{.2}{2^{.767}}$

$$\log K = \bar{0}.92986$$




By means of these two constants the value of $S_0$ is calculated to be 18.88 gm. per 100 gms. solution. This value is somewhat lower than the ordinary solubility of water in n-butyl alcohol at 25° C. which was found to be 19.5 per cent. If however we consider the figure 18.88 as representing the tendency of water to dissolve in pure n-butyl alcohol there is every reason to expect a lower value of solubility than the ordinary value.

We have applied the ideas of capillarity to explain the retention of water by silica gel from solutions of water in n-butyl alcohol. Considerable difficulties present themselves however in extending

these views to systems where the components of the solution are miscible in all proportions. The main difficulty is in finding a value to ascribe to the interfacial tension. For example, acetic acid and benzene are miscible in all proportions at ordinary temperatures. Nevertheless it is believed that in a capillary tube which is wetted by acetic acid in preference to benzene and which is sufficiently small in diameter, acetic acid may exist as a separate phase in the tube in contact with a solution of the acid in benzene. It is even believed, according to this view, that capillary condensation of both the gaseous phase and from solution may occur at temperatures above the critical temperature. Discussion of this point would carry us beyond the scope of this article but it may be mentioned that considerable evidence has been collected in support of this view.

## Summary

1. A brief discussion of the capillary theory of adsorption of vapors is given.

2. A new adsorption formula is derived from the thermo-dynamic laws of capillarity.

3. An empirical adsorption formula is applied to both gaseous and solute adsorption, in which is brought out the fact that the surface tension of a liquid varies with the radius of curvature.

4. The laws of capillarity are applied to explain adsorption from solution in a qualitative manner.

5. The adsorption of water from n-butyl alcohol is studied and a method shown of evaluating the tendency of water to dissolve in pure n-butyl alcohol.

## Discussion

DR. CHANEY: The difficulty of a deferred discussion of this kind is that some of you may not have heard the original paper and to others the subject matter may not be clearly in mind.

One thing to which I wished to call attention, however, is that the monistic view point of Dr. Patrick in ascribing adsorptive activity solely to capillary phenomena is the natural and logical result of the material—silica gel— with which he has been working; whereas the dualistic viewpoint as to the behavior of solid absorbents which we developed in our paper upon activated carbon, namely the existence of a chemical or "specific" factor in addition to purely capillary phenomena, was the equally logical and inevitable result of the material which we were studying.

We agree with Dr. Patrick that in the case of silica gel the "specific" or selective factor is very weak, and the predominating influence in the behaviour of the gel is the physical nature of its capillaries. This accounts for the success with which Dr. Patrick has been able to treat his data from the purely physical viewpoint. Silica gel is the ideal material in which to study capillary phenomena as it offers a minimum of selective chemical disturbance, which made it easy to lose sight of the latter altogether. That such selectivity, however weak, does exist, is shown by the power which water has to displace adsorbed benzol from silica gel, whereas the exact reverse is true with respect to carbon.

In the case of activated carbon however, the specific factors become so intensified and predominating that it is no longer possible to overlook their presence or significance.

We may say therefore that there is no inherent conflict between Dr. Patrick's observations and our own. The difference is that his treatment represents a special and limited case of adsorptive activity in which he is able to dismiss the chemical polarity of his adsorbent as a negligible quantity and get reasonably satisfactory results based purely upon mathematical considerations as to capillary diameters.

We differ with him only if he attempts to make a general case out of a special one and to extend his conclusions to adsorptive phenomena as a whole and to the behavior of such adsorbents as carbon in particular. Dr. Patrick however admitted that the adsorption of solids did not come within the scope of the capiliary theory. Obviously a theory of adsorption which does not include the absorption of dissolved solids from solution, or, presumably, of colloids is very limited both from a theoretical and industrial standpoint. What we wish to call attention to here is that even in the adsorption of liquids, Dr. Patrick's theory of capillary adsorption represents a special case, limited to silica gel, and we believe his explanation would fail to account for the behavior of a highly specific adsorbent such as carbon.

Attention might be called also to the fact that when Dr. Patrick rationalized his vapor adsorption curves by calculating the liquid volumes of his absorbed vapors the success of this operation was probably due to the fact that the limiting factor in the absorption of a given vapor was the total available capillary volume. In this case the total absorptive capacity for the various gases would neces-

sarily correspond with the specific volumes of the latter in liquid state, regardless of whether the condensation was caused by specific polar forces or by capillary depression of the vapor tension. If this correctly states the case, the rationalization of the data affected by these calculations throws no light at all upon the question of whether the forces operating to cause the adsorptions were primarily capillary or chemical.

PRESIDENT HOWARD: Is there further discussion of this paper?

SECRETARY OLSEN: I would like to ask Dr. Chaney about his statement that silica gel has no specific adsorptive capacity. Do you mean that it will not adsorb a specific substance?

DR. CHANEY: What I referred to there was the point that we brought out in our own paper, namely, that carbon for example has a retentivity for such material as toluol of the order of from 30 to 50 per cent, and that in the case of silica gel the retentivity is of the order of one and a half per cent. That is of a relatively negligible order. What specific character the silical gel did have, was selective for water rather than for hydrocarbons and organic derivatives. Yet while quantitatively this seems to be very small, from a practical standpoint it is quite sufficient to secure a completely selective absorption of water and rejection of such a material as benzol when silica gel is placed in contact with both.

SECRETARY OLSEN: This shows that silica gel adsorbs sulphur from oil. Is not that a selective adsorption from some sulphur compound?

DR. CHANEY: I am not familiar with the data on which we would define the specific character of silica gel for sulphur. There may be some materials for which silica gel is highly specific. We have no data on this by our methods except with such materials as water, and the commoner vapors.

SECRETARY OLSEN. If you should treat the same oil with carbon, would you then get an adsorption of sulphur?

DR. CHANEY: Yes.

SECRETARY OLSEN: Just as silica gel does?

DR. CHANEY: Yes.

SECRETARY OLSEN: In other words, you could replace the silica gel by carbon in that operation?

DR. CHANEY: Yes.

PRESIDENT HOWARD: Is there any further discussion on this paper? If not I declare the discussion closed.

# ACTIVATED CARBON—ITS EVALUATION, MANUFACTURE AND USES

By FREDERICK BONNET, Jr.

Read at Wilmington, Del., Meeting, June 20, 1923

The peculiar property of charcoal to take up gases, to destroy noxious odors and to remove coloring matter from solutions has been known probably for centuries, and has piqued the curiosity of a great number of investigators. In the early part of the last century De Saussure [1] pointed out that freshly heated beechwood charcoal took up gases to a remarkable extent, and seemed to condense them upon itself. Some years later Hunter [2] carried out similar experiments. While he did not get the same values as did Saussure, due no doubt to a difference in preparing the charcoal, both investigators found that the more readily condensible gases are taken up to a much greater extent.

In other words, the adsorption of a gas by charcoal, or, in fact by all substances, is roughly parallel to the ease with which they are condensed to their liquid state,[3] as shown by the following table:

TABLE I

Comparison of Adsorption with Ease of Condensation of a Gas

| Gas | Boiling Point °C. | Crit. Temp. °C. | c.c. Gas Adsorbed 0° C. per Gram of Charcoal | |
|---|---|---|---|---|
| | | | Wood at 10 c.m. Pressure | Cocoanut at 76 c.m. |
| Helium | −268 | −267 | .. | 2 |
| Hydrogen | −253 | −241 | 0.3 | 4 |
| Nitrogen | −196 | −149 | 1.5 | 15 |
| Carbon monoxide | −190 | −136 | .. | 21 |
| Oxygen | −183 | −119 | 2.0 | 18 |
| Argon | −186 | −117 | .. | 12 |
| Carbon dioxide | − 78 | +131 | 20.0 | .. |
| Ammonia | −33.5 | +130 | 30.0 | .. |

[1] *Gilb. Ann.* **47**, 113 (1814).

[2] *Phil. Mag.* (4), **25**, 364 (1863); **29**, 116 (1865).

[3] *J. Ind. Eng. Chem.*, **11**, 422 (1919).

Moreover, the different adsorptive capacity of charcoal for various gases is more effective at low temperatures; and Dewar [4] made use of this property in isolating the rare gases helium, neon, etc., occurring in the atmosphere. He also produced very high vacua by adsorbing residual gases on activated charcoal.

The war greatly stimulated the development of activating carbons for gas masks and this phase has been very fully described by Lamb, Wilson and Chaney.[5]

## Decolorizing Carbons

Turning now to the subject of decolorizing carbons, 150 years ago Lowitz [6] pointed out that charcoal has the power to deprive most coloring liquids of their coloring matter. He quite successfully removed the color from solutions of cochineal, indigo and claret. A few years later (1794) we find an English sugar refinery actually using charcoal to remove color.

The early success in 1808 of beet sugar manufacture by Delessert was largely due to the use of decolorizing charcoal. However, a few years later, in 1812, bone black or bone char was discovered. As a decolorizing agent, especially for sugar, this was so much more effective than the ordinary wood charcoal, that the use of bone char became an established procedure in the refining of sugar. In fact it became quite generally to be considered an absolute necessity for the making of good sugar. Although this idea is no longer tenable, owing to the great improvements made in the production of vegetable chars and the successful large scale trials which have recently been made with them, bone char is still largely used by refiners.

In spite of the early and continued success of bone char, vegetable chars as decolorizing agents were not forgotten. As early as 1836 Boettcher recommended the use of brown coal, or lignite, a natural carbonization product of vegetable origin, for refining sugar intended for the East Indian market, owing to the religious scruples of the Hindus regarding sugar made with the aid of bone char, a substance of animal origin. In the sixties, the subject of vegetable carbons was revived again and created a great deal of spirited discussion. Since then much has been written and many patents have been taken out covering the various phases of this interesting

[4] *Proc. Roy. Soc.*, **74**, 122 and 127 (1904).

[5] *J. Ind. Eng. Chem.*, 11, 420 (1919).

[6] Lippman, *Geschichte des Zuckers.*

subject. The greatest variety of raw materials have been subjected to charring and hardly any natural or waste product has escaped investigation. In fact a review of the literature and patent applications of the various countries shows that countless attempts have been made to determine the causes of this phenomenon and so to treat various carbonaceous raw materials that the resulting char will show a maximum decolorizing power while retaining physical properties which would make its technical application successful.

## Theoretical Considerations

The value of a carbon or char is judged by its ability to take up and hold gases or dissolved substances, i.e., its adsorptive capacity. The cause of this phenomenon has been very extensively studied and the generally accepted theory is that based on the well known deductions of Willard Gibbs (1874).

Gases, as well as liquids or solids in solution, are adsorbed on the surface of the adsorber, due to a change in the interfacial tension between the adsorber and the adsorbed material. When, therefore, carbon or other adsorber is applied to a solution, for example, the dissolved substance will be concentrated at its surface until the work done in withdrawing the solute from solution is equal to that represented by the lowering of the surface tension at the adsorber, i.e., if there are present in solution small amounts of substances having a lower surface tension than the solvent (as is usually the case in technical work) then these will be concentrated at the surface until a corresponding lowering of the surface tension has taken place and an equilibrium has been established.

In general, therefore, the larger the surface of the adsorber exposed to a given solution the more solute will be withdrawn from the solution. Again, relatively more solute will be extracted from a dilute solution than from one more concentrated. The presence of the adsorber causes a new equilibrium to be established in the solution. Freundlich [8] expressed this by the following equation— $X/M = KC^{1/n}$; in which $X$ equals grams of solute (or gas) adsorbed, $M$ equals the grams of adsorbent, and $C$ equals the concentration (grams per liter) of solute in solvent after equilibrium. $K$ and $n$ are constants, the numerical values of which depend on the adsorber, the solvent, the solute and other conditions of the experiment. For

[8] Freundlich, "Kapillarchemie."

gas adsorption $C$ is the pressure of the gas after equilibrium has been established.

## Explanation of Adsorption

The exact cause of adsorption, i.e., why substances are adsorbed has been much discussed. The difficulty in proving the various theories suggested lies in the practical impossibility of measuring either directly or indirectly the interfacial surface tension. However, recently Gurwitsch [9] has suggested that the heat of adsorption is a measure of the adsorptive forces involved. While not questioning the correctness of the thermo-dynamic theory of Gibbs he considers adsorption as one of the manifold physico-chemical phenomena of attraction, which molecules of all chemical compounds, even the so-called saturated ones, possess with reference to other molecules. From experimental data he finds that the greatest amount of heat is evolved by such liquids which from a chemical standpoint are the most active, e.g., unsaturated compounds, and those containing oxygen and nitrogen which have multiple valencies, while the least heat is evolved with saturated and symmetrical compounds like carbon tetrachloride. The process taking place he explains as follows:

When an adsorber comes in contact with a solution it attracts the molecules of the solute as well as the solvent to its surface, which may be considered as consisting of condensed molecules or films, the dimensions of which are determined by the reaction radius of the adsorber. The ratio in which the molecules of the solute and solvent occur in this film is determined by (1) amounts of both molecules in the solution, and (2) the energy with which these are respectively adsorbed by the solvent.

Therefore, if one and the same adsorber is used with solutions of the same concentration of the same solvent, the solute with the greatest adsorbability will be adsorbed most. If on the other hand we have the same solute in the same concentration but in different solvents then the solute in the solvent showing the least adsorption will be adsorbed most. There seems to be a rivalry between the molecules of the solvent and solute, each striving to condense itself on the surface of the adsorber. These two rules, together with the general character of physico-chemical attraction energy involved, make it possible to predict many of the ordinary adsorption phe-

[9] *Kolloid Ztsch.*, **32**, 80 (1923).

nomena. For example, when mixtures of acetic acid with benzol or toluol are treated with an adsorbent, those with a high initial concentration of acid show an increase in acidity and vice versa, those with low initial concentration of acid show a decrease.[9] The same holds true with other solutions.

A 94.7 per cent alcohol solution after filtering through an activated carbon showed 98.9 per cent, while a 9.16 per cent alcohol solution after filtering showed only 7 per cent. Again a mixture of 96.1 per cent benzol, and 3.9 per cent of chloroform had an initial specific gravity of 0.8898, and after filtering only 0.8880, i.e., the chloroform was adsorbed; while one of only 4.45 per cent benzol and 95.55 per cent chloroform with an initial specific gravity of 1.4348 increased to 1.4364, i.e., the benzol was adsorbed. It is rather difficult to explain such positive and negative selective adsorption by the Freundlich conception.

While theoretical discussions are important and profitable in supplying a viewpoint, the results of theoretical experiments carried out under more or less ideal conditions with pure substances are hardly directly applicable to the problems of the technical chemist. He is confronted for the most part by a complicated mixture of heterogeneous substances, the chemical constitutions of which are unknown to him. Even the matter of determining the concentration of the substances in solution is quite impossible. Moreover, the comparatively simple adsorption on the surface of the adsorber becomes quite involved when, owing to the adsorption of oxygen, for example, the adsorbed gas or solute enters upon chemical reactions. Again the solute may be concentrated to such an extent that it separates from the solution and covers the surface of the carbon, filling up the pores and preventing an effective adsorption taking place, e.g., in certain cases with oils the free fatty acids or soaps separate at the surface, preventing any proper degree of decolorization. The concentration of the free fatty acids or soaps must then be reduced below the point where separation at the surface takes place before very efficient decolorization can take place.

Another example of change at the surface of the adsorber is in the case of certain dyes, the basic portion of which is adsorbed while the anion remains wholly in solution. Moreover, carbon itself, as does its ash in some instances, acts catalytically upon certain substances. For example, phosgene is hydrolyzed into hydrochloric acid and carbon dioxide in the presence of moisture. The same is

true of trichlormethylchlorformate, "superpalite." These examples will indicate a few of the side reactions which can and do at times take place at the surface of the carbon, in addition to the phenomenon of pure adsorption.

## Evaluation of Activated Carbons

The evaluation of activated carbons for technical purposes is an important matter, not only from the standpoint of the user but from that of the manufacturer as well. It is important when discussing activating carbons to keep in mind that, starting with one and the same raw material, chars of varying degrees of activation or adsorption can be prepared. The manufacturer is interested in obtaining the highest degree of activation with a minimum loss of material and at a minimum cost. The user is interested only in so far that, other physical characteristics being equal, that carbon with the highest adsorptive capacity will do the most work when applied to his particular problem.

In the case of gas adsorption the so-called accelerated chlorpicrin test is now commonly used.[10] Essentially it consists in passing a stream of dry air containing 7,000 parts per million of chlorpicrin at a rate of 1,000 c.c. per square cm. through a 10 cm. layer of the carbon until the first trace begins to come through. The time in minutes of breaking down measures the value of adsorptive capacity.[11]

Government plant production during 1918 of activated carbon for gas masks averaged about 18 minutes while the last two months of production gave an average of about 35 minutes. Large-scale units frequently produced 50-minute material while in the research laboratory a product running as long as 70 minutes on the foregoing test has been made. The most suitable material for gasolene adsorption is a 50–60 minute char, which material will adsorb 10–15 per cent of its own weight and will retain the salable vapors for subsequent recovery.[12] For solutions a definite weight of carbon is shaken with an empirical and more or less standard test solution, e.g., methylene blue, eosin, iodine, molasses solutions, etc., and a colorimetric determination of the filtrate indicates how much color the given weight of carbon has removed. The various types of

[10] Ref. (5), also *Chem. Met. Eng.*, 24, 156 (1921).
[11] *J. Ind. Eng. Chem.*, 11, 420 (1919).
[12] Ref. (10).

colorimeters technically used for measuring the color of such solutions have been discussed by Sanders.[13]

In cases where there are no disturbing side reactions, the adsorption of color from solutions can be expressed by the Freundlich equation $X/M = KC^{1/n}$. Dr. F. W. Zerban, in a paper presented at the fall meeting of the American Chemical Society in New York, 1921, showed conclusively that not only was the color removed from sugar or molasses solutions according to this equation, but that by obtaining the carbon isotherms in this way, i.e., the effectiveness at different concentrations, the carbons behaved differently. Thus, while one carbon showed an excellent efficiency at a low concentration, it was not as good as another carbon showing a low efficiency at the low concentration and a high efficiency at higher concentration. In evaluating a carbon as to its decolorizing power it is not sufficient merely to determine its decolorizing power at one concentration, but its action on a range of concentrations is necessary to give an adequate idea of its behavior.

More recently M. T. Sanders, in a paper before the American Chemical Society, at its New Haven meeting in April, 1923, has quite fully discussed this matter and has shown that the use of the Freundlich equation enables one to determine the relative decolorizing capacity of various carbons with a minimum of tests. He also shows how the isotherms are to be interpreted, and makes clear the fact that whenever it is possible the use of the counter-current method of decolorization will reduce the amount of carbon consumed by a given quality of solution.

While the decolorizing or adsorptive capacity of a carbon is important, there are other factors which from a technical standpoint are quite of equal importance. For example, the matter of fineness, filterability, structure, neutrality, moisture, ash, water and acid solubles, etc., are large factors which determine the technical usefulness of a carbon.

The fineness of a carbon cannot be determined with any degree of accuracy by dry screening, and wet screening must be resorted to to get consistent results. This test is carried out as follows:

Five grams of a dry sample of carbon are weighed into a beaker and thoroughly wet down with water so that it may be poured on to the screen. A quiet stream of water is then run into the screen and the fine material washed through. The portion remaining on the

[13] *Chem. Met. Eng.*, 28, 541 (1923).

screen is transferred by means of water to a weighed Gooch, which is dried and weighed. The following table shows the fineness referred to a 300-mesh screen for several commercial vegetable chars. The fineness of the material is important both from the standpoint of decolorization as well as that of filterability, which in turn depends on the structure and uniformity. If a carbon is ground very fine and the particles are very uniform it may be difficlt to filter, and any gain or advantage due to the larger surface exposed, in adsorptive capacity, is lost and often more than lost by the difficulty experienced in filtration.

TABLE II

RESULTS OF EXAMINATION OF COMMERCIAL VEGETABLE CHARS

| Carbon | Per Cent Through 300-Mesh | Reaction | Decolorizing Power | Per Cent Ash | Per Cent Water Solubles | Per Cent Acid Solubles | Approximate Weight Per Cu. Ft. Dry |
|---|---|---|---|---|---|---|---|
| *A* . . . . | 50 | Neutral | 75 | 27 | 0.75 | 2.0 | 32 |
| *B* . . . . . | 46 | Neutral | 68 | 9 | 0.26 | 4.63 | 21 |
| *C* . . . . . | 48 | Neutral | 53 | 7 | 0.11 | 4.73 | 25 |
| *D* . . . . | 42 | Neutral | 66 | 1 | 0.21 | 0.81 | 20 |
| *E* . . . . . | 42 | Acid | 90 | 1 | 0.21 | 0.81 | 20 |
| *F* . . . . . | 62 | Neutral | 71 | 1.43 | 0.00 | . . | 17 |
| *G* . . . . . | 84 | Neutral | 64 | 4.7 | . . | . . | . . |
| *H* . . . . | 51 | Neutral | 56 | . . | . . | . . | . . |
| *I* . . . . . | . . | . . | . . | . . | . . | . . | 62.7 |

The comparative filtering of carbon can be approximately measured in the laboratory by mixing say 10 grams of the carbon with 800 c.c. water and filtering under a definite vacuum on the 3-in. Buchner funnel fitted with a piece of standard filter paper. The time taken with a stop watch to filter the 800 c.c. gives the filterability. Usually five tests are made and the average taken. This is of course merely an approximate laboratory method and does not prove that the best filtering carbon will give equally good results on the plant, but it does give some idea of the structure, fineness and uniformity of one carbon as compared with another.

The neutrality of a carbon is determined by testing the water extraction of the carbon (10 grams carbon, 200 c.c. water heated to boiling) with litmus. It will be noted that a slightly acid carbon, the acidity of which may be due to insufficient washing in manufacture, or due to hydrolysis of such salts as iron or aluminum chloride, may show a very high decolorizing power, owing to the

acid present. (See Table II.) Carbon D and E are the same, the only difference being that the acid in E has been removed in D.

The moisture in the carbon is largely due to adsorption from the atmosphere. Heating at 140° C. for 16 hours is usually sufficient to drive it out. All tests on carbon should be made with the dry material, although several cases have come to our attention where the carbons were weighed as received. Since good carbons adsorb from 10 to 15 per cent moisture, tests made on anything but dry material are necessarily misleading.

The ash is determined in the usual way by weighing out a suitable amount of carbon (2 grams), drying and igniting. The ash content of various commercial carbons runs from a few per cent to almost 90 per cent in the case of bone char (Table 2). Water solubles are usually determined by weighing 10 grams of carbon and extracting four times with 200 c.c. of water, heated to the boiling point, whereupon the carbon is transferred to a Gooch, dried and weighed. The difference in weight represents the material dissolved. Acid solubles are determined in a similar way, only instead of water a 20 per cent solution of hydrochloric acid is used.

Another factor of interest so far as technical results are concerned is toughness or resistance to breaking into finer particles when in use. Some commercial carbons, while showing very good adsorptive capacity, are so soft and so friable that they rapidly disintegrate when handled on the plant. The ideal carbon would be one without water or acid solubles, with a very high adsorptive capacity, possessing such structure that it gives a very high rate of filtration and such hardness or toughness that it could be handled without appreciable loss or disintegration during use, and which could be economically revivified without losing any of the above qualities.

It is doubtless true that bone char has maintained its position in the sugar industry because of its hard, granular structure and that while even the older vegetable chars showed a higher decolorizing power they were too soft. In a recent article Avot [14] gives some figures obtained on large scale tests at sugar refineries which show that the best vegetable decolorizing carbons as made to-day possess a decided advantage over bone char and that it is his opinion that many of the present refineries and certainly most of the new ones of the future, will substitute wholly or in part the powerful vegetable carbon for the less efficient bone char.

[14] *Facts About Sugar*, 16, 170 (1923).

## Manufacture of Activated Carbons

As mentioned above a great number of patents for the manufacture of activated vegetable chars have been taken out, since the early eighties. As bone char with approximately 10 per cent carbon was so effective as the decolorizing agent, it was natural that the early investigators attempted to produce similar material by mixing with cheap carbonaceous matter, inert substances like chalk, flint, pumice, etc., before charring, the idea being to have these admixtures serve the same purposes as does the calcium phosphate in bone char, namely a skeleton on which carbon particles could be deposited in an amorphous state so that a much greater surface of carbon would be exposed, at the same time producing a more porous product with good physical properties.

Instead of adding inert substances, a simpler and usually less expensive method is to choose such initial raw material which already has the skeleton material in it; in other words, shows a high percentage of ash, chiefly silica or lime salts. As an example of such raw materials we might mention certain grasses, rice hulls, barley awns, etc. The decolorizing power of chars made by simple carbonization of these materials is not very marked but can be greatly developed by removing the silica, lime or lime salts from the resulting char. In the case of rice hulls, boiling the char with water containing 20 per cent of caustic soda based on the weight of the char gives a very good carbon, containing only 9 per cent ash as compared with 50 per cent before extraction. In choosing raw materials such as grasses, rice hulls, etc., it becomes necessary to deal with very bulky material, which for large-scale operation becomes costly, even if the raw material can be obtained in sufficient quantity. A much better raw material is lignite, a partially carbonized product of vegetable origin which occurs native in enormous deposits.

In the manufacture of an activated carbon either for gaseous adsorption or for decolorizing purposes, certain facts must be clearly kept in mind. If the carbonaceous material is heated too rapidly or at too high a temperature substances are formed during initial distillation which first condense on the surface of the carbon and which then if the temperature is sufficiently high break down and leave a residual gas or graphitized carbon on the surface which destroys the adsorptive power of the amorphous carbon beneath.

Moreover, it is most difficult to remove by any subsequent oxidation. To prevent this action during heating a mild form of oxidation in some form is necessary. Experimentally some good carbons have been obtained by heating the raw material in the presence of a small amount of air or carbon dioxide. The disadvantages in this procedure are that although the furnace temperature may be sufficiently low to prevent graphitization local heating may occur due to the exothermic reaction between the carbon or carbon compounds and the oxygen of the air. Carbon dioxide is better in this respect, but the use of steam, which produces an endothermic reaction, gives the best product.

## Procedure

The technical preparation of a carbon is carried out essentially in two stages, viz., heating at a relatively low temperature to form the amorphous base carbon, and removal of hydrocarbons adsorbed by this carbon to increase the porosity of the material. These two reactions are sometimes carried out in the same furnace.

The ground raw material is fed into a revolving retort, slightly inclined, in a comparatively thin layer so that contact of hydrocarbon vapors with hot carbon is avoided so far as possible and the vapors are removed before cracking temperatures are reached. As the carbon travels down the tube the temperature rises so that by the time it reaches the steam zone the temperature is right for the scouring action of the steam to become effective. After it leaves the tube the carbon is termed rotite. The next steps in the procedure are to grind the carbon to size and to acid treat it in order to remove part of the ash and impurities, but especially to open the pores and thus expose larger adsorptive areas of the carbon. After the acid treatment and most thorough washing on the countercurrent system the material is dried and packed.

The removal of the hydrocarbons by distillation and oxidation has for its main purpose the activation of the carbon, but there is some oxidation of the primary carbon as well, which up to a certain point is an advantage since it releases some of the cavities or pores in the charcoal and thus increases its effective surfaces.

From what has been said it is obvious that the principles underlying activation are so to choose conditions as to oxidize the hydrocarbons rapidly while the primary carbon is oxidized slowly. This is not always easy to accomplish since the hydrocarbons are for the

most part enclosed within the primary carbon particles. Moreover, a sufficiently high temperature must be maintained to cause the rapid oxidation of the hydrocarbons but it must not be so high that it causes an unnecessary and wasteful oxidation of the primary carbon as well. For air oxidation the optimum temperature lies between 350 and 450 deg. C., while with steam between 850 and 1,100 deg. C. Air oxidation has the advantage of operating at a comparatively low temperature, but the local overheating due to the exothermic oxidation causes too great a loss of the primary carbon and an actual loss in the effective surface occurs before all the hydrocarbons have been oxidized. Carbons of the highest activation cannot be prepared in this way. Steam activation has the disadvantage of operating at high temperatures with consequent technical difficulties of heat regulation, choice of furnace material, etc., but it has the great advantage of the endothermic reaction above referred to so that the hydrocarbons can be removed without excessive loss of primary carbon.

## Recent Developments

Mention must be made of some recent developments abroad which seem to give promise of producing a hard, dense charcoal of excellent quality. The raw material is first treated with sulphuric acid, zinc chloride, hydrochloric acid, etc. During carbonization these substances cause the hydrogen and oxygen to be removed practically as water, no hydrocarbons being formed and a dense hard carbon being left behind. The sulphuric acid method has been tried in England, while the hydrochloric acid and zinc chloride methods have been used in Germany. All three use wood as the initial raw material and in each case a product has resulted which is better than that made without first processing with dehydrating agents.

## Uses of Activated Carbon

In closing this very general survey of activating carbons, it may be of interest to summarize briefly some of the uses to which the material has been put.

*Gas and Vapor Adsorption.*—The adsorptive capacity of a good activating gas carbon is high, especially at low temperatures, that at the temperature of liquid air it will bring 100 times its own volume of air at atmospheric pressure down to a pressure of a few

mm. mercury in a few seconds. Even at ordinary temperature carbon made on a large scale will absorb half its own weight of certain toxic gases while samples prepared in the laboratory have absorbed more than their own weight.[15] The chemical stability of carbon is excellent and since it adsorbs all gases and vapors to a greater or less extent it is really a universal adsorbent.

*Gasolene Recovery from Natural Gas.*—Burrell states as a result of very large scale tests that the charcoal process for gasolene recovery produces higher yields and a better grade of gasolene. It does not require heavy installation costs and can be operated more cheaply than either the compression or solvent method. The apparatus has longer life and is not subjected to inefficiency due to wear. Its adaptability to field conditions is enhanced by the fact that it operates on either lean or rich gas and either at high or low pressure.[16] High test gasolene was prepared in Europe by this means for airplane and other war uses.

The use of activated acrbon in medicine made great strides during the war, and Kraus and Barbara [17] recommend carbon as an excellent adsorbent for toxins. In army camps during the World War diarrhea, dysentery, cholera and other intestinal diseases were almost wholly controlled by its means.[18] It also has been used most successfully in the case of phenol poisoning. Other medicinal uses, especially in surgery in the treatment of odorous pus-forming wounds, might be mentioned. A suggested use is the concentration of vitamines. The largest use at present is doubtless in the sugar refining industry, both cane and beet, which have already been mentioned.

Other uses are in candy and syrup manufacture for recovering wastes. Fruit canning, preparation and refining of glucose, maltose and lactose, table oils and foods, lard and butter substitutes, gelatine, glue, alcohol, pharmaceutical products like quinine, caffein, organic acids like lactic, citric and tartaric, cream of tartar for baking powder, photographic chemicals, etc. It may be interesting to mention that in the case of purification of the alkaloids, the alkaloids may be adsorbed on the carbon and then subsequently removed therefrom by means of a suitable solvent.

[15] Ref. (5).
[16] *Chem. Met. Eng.*, **24**, 156 (1921).
[17] *Deutsch Med. Wochensch* (1915).
[18] *Bull. Pharm.*, 393 (1913).

The above list is in no way complete and is merely indicative of the growing uses to which activated carbons are being put. Its really wonderful properties are gradually being recognized and it is the chemical engineer to whom we must look to develop technical means for more successfully applying it and extending its uses.

WILMINGTON EXPERIMENTAL LABORATORY,

ATLAS POWDER COMPANY.

# THE PROPERTIES OF ACTIVATED CARBON WHICH DETERMINE ITS INDUSTRIAL APPLICATIONS

By N. K. CHANEY, ARTHUR B. RAY and ANCEL ST. JOHN

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## I. Principles of Activation and Nature of Active Carbon

In 1919 the senior author published [1] (1) a preliminary account of investigations eventuating in the processes for making gas mask carbon which were adopted and exclusively employed by the U. S. Chemical Warfare Service during the war. This paper summarized the conceptions as to the nature of active carbon and the theories of activation which had proved successful as a working hypothesis in directing this work. Since then the investigation of both the technical and theoretical phases of carbon activation has been continued in this Laboratory, and the scope of the work broadened to cover the general problem of the physical nature and interrelationships of the various forms of carbon. New lines of attack have been employed, including the development of special methods and technique for utilizing X-ray crystallographic analysis.

The general theory of carbon activation set forth in the 1919 paper referred to may be summarized briefly as follows:

*First.* In addition to the recognized forms of graphite and diamond two forms of carbon possessing distinctive physical properties are postulated: (1) to explain the observation that free carbon liberated from its compounds below a certain critical temperature range[2] was either active or capable of yielding active carbon while free carbon liberated at higher temperatures (approximately 600–700° C.) was both inactive and incapable of activation by any known means; (2) to account for the unique differences in chemical reactivity and adsorptive power of the high and low temperature forms of carbon after treatment by activating processes.

[1] Numerals refer to a bibliography at the end of the paper.

[2] This statement refers to the temperature range in which chemical decomposition occurs and not to the temperature to which the carbon may have been subsequently raised. Thus chemical constitution is significant to the extent that it determines the decomposition temperature.

*Second.* The formation in all "primary" carbons, such as low temperature chars and cokes, of a peculiarly stable adsorption complex between the active carbon and the residual hydrocarbons was postulated for the following reasons: (1) this would logically result from the unique adsorptive power predicated of active carbon; (2) it accounted for the saturated and relatively non-adsorptive properties of ordinary chars; (3) it accounted for the fact that carbon deposited at low temperatures from CO and other non-hydrocarbon compounds was highly active and required no "activation"; (4) the persistence of residual hydrocarbons in chars heated far above the normal decomposition temperature of the hydrocarbons was explained as a result of the protective mechanism of such adsorption; (5) finally, it was in harmony with all known facts and processes of activation, and directly suggested the most effective principle of all, namely, that of selective chemical attack upon the adsorption complex by means of controlled oxidation.

Thus the features which distinguished the original disclosures of the Chaney processes of carbon activation were (1) a clear-cut differentiation for the first time between the inherently activatable and the inactivatable forms of carbon, and recognition of the fact that the controlling factor in determining whether carbon would assume the activatable or the inactivatable form was the temperature at which the elementary carbon was liberated from its compounds; (2) the concept of the activatable forms of carbon (so-called "primary" carbon) as consisting of a uniquely stable complex of "active" carbon and adsorbed hydrocarbons, and the activation process as consisting of the separation of these adsorbed hydrocarbons from the active carbon by means of a selective *chemical* reaction carried to a definite *quantitative* conclusion.

Because of their deficiency at precisely these points, the vague disclosures of the prior art proved of no practical value to the allied chemists. None adequately defined the conditions essential to the production of the activatable forms of carbon in quantity under commercial conditions, nor taught that the activating environment should be employed in a well-defined manner to achieve a specific chemical reaction. Chemists of the French Army Service actually experimented with a process employing "high temperature steam" said to have been used in Russia and definitely rejected it as giving an unsatisfactory product.

Further to illustrate the vital and complementary character of

these principles in the development of successful methods for the large-scale production of highly active carbon the following is cited:

Early in 1918 the U. S. A. Chemical Warfare Service was under heavy pressure to find a substitute for the inadequate supply of cocoanut and similar shell carbon. They were already employing the Chaney processes of selective oxidation, by both air and steam methods as applied to properly prepared cocoanut and wood charcoals. Acting upon information from the National Carbon Company's Laboratories that anthracite was capable of activation, their engineers secured a retort from a gas company in Springfield, Mass., filled it half full of 8–10-mesh anthracite coal of a selected grade, introduced a steam pipe at the bottom of the retort, raised the temperature to 900° C. and tried to activate the anthracite. The outcome was a complete failure. Samples of the anthracite from the retort when later returned to our laboratory were found to be not only inactive but absolutely incapable of activation even under ideal laboratory conditions; whereas the original raw anthracite was readily activated under precisely the same conditions. In the light of our two postulates above the explanation was obvious enough. The heating of the retort had been carried on in such a manner that large sections of the anthracite had reached a high temperature while other portions were still undergoing active distillation at lower temperatures. The hydrocarbon vapors distilling from the low temperature sections had then passed through and been "cracked" upon the more highly heated anthracite particles at temperatures above the critical decomposition temperature range and had been deposited in the pores of the anthracite as inactive carbon. As this deposit of inactive carbon was highly resistant to oxidation, the application of "selective" oxidation processes to the "gas-treated" anthracite merely burned away the active carbon (together with the hydrocarbons) and left the inactive form and the ash as the end-product. Equipped with this information our engineer, Mr. V. C. Hamister, then employed an inclined retort and by properly controlling the heating, the steam concentrations, and the circulation of hydrocarbon vapors, worked out a routine method which permitted the manufacture of a moderately good gas mask carbon from anthracite in ton lots. By using this carbon (Batchite) mixed with the better grade shell carbon in ratios of about 1 part in 3 a serious shortage of gas mask carbon was averted. This example is cited because it so clearly illustrates the inadequacy of certain

earlier statements as to the heating of carbon at high temperatures in the presence of steam, and shows why such references led to no fruitful results.

In addition, however, to the practical coordination of the several principles underlying these two postulates as to the general nature of activation the Chaney disclosures involve a third principle which is specific to the preparation of the highest types of gas adsorbent carbons. This principle arises from the fact that military uses and most industrial applications involving the adsorption of gases and vapors place a heavy premium upon the maximum of adsorptive capacity per unit *volume* of adsorbent.

As a result it may be shown that there must exist a definite critical density or porosity of adsorbent, corresponding to its maximum capacity per unit of volume. Other things being equal, any departure from this critical density in either direction impairs the potential adsorptive capacity of the carbon. The reasoning is obvious. If the porosity approaches zero, the available exposure of active carbon becomes negligible. A space entirely filled with carbon atoms has no room for adsorbable molecules. On the other hand, as the porosity approaches 100 per cent the mass of active carbon per unit of volume approaches zero, and its adsorptive capacity falls off accordingly. Between these two extremes there is a certain density or porosity in which the maximum mass of active carbon is most effectively exposed. It has been experimentally determined for steam-activated shell carbon that this critical apparent density is about 0.4 (for 8–10-mesh granules) or that the desired porosity of the individual granule should be 66 per cent.

The actual value of this "critical density" was determined by observing the density at and below which the adsorptive power of the carbon per unit of *mass* became constant. As a matter of observation all highly activated carbons having a density of less than 0.4 (for 8–10-mesh granules) tend to approach a substantially constant adsorptive capacity per unit *weight* of carbon, which means that their capacity per unit volume then becomes a simple function of their density.

This is illustrated by the data in the following two tables taken from reports by Chaney in 1918 to the Chemical Warfare Service.

Table 1 shows the capacity of certain typical charcoals for adsorbing chlorpicrin when completely activated.

The capacity $S^1$ is the number of minutes service on the C.W.S.

standard tube test. *SW* is the adsorptive capacity expressed as the weight of chlorpicrin absorbed by 1 gram of carbon under the same test conditions. A.D. is the apparent density of 8–10-mesh carbon granules.

TABLE 1

| Source of Carbon | $\frac{(1)}{\text{A.D.}}$ | $\frac{(2)}{S^1}$ | $\frac{(3)}{S^1/10 \text{ A.D.}}$ | $\frac{(4)}{SW}$ |
|---|---|---|---|---|
| Cocoanut | 0.430 | 955 | 222 | 0.76 |
| Babassunut | 0.330 | 770 | 233 | 0.82 |
| Cedar | 0.103 | 240 | 234 | 0.78 |
| Sycamore | 0.097 | 227 | 234 | 0.79 |

As shown in column (3) the ratio of the service time or gas capacity to the apparent density for fully activated chars of less than 0.4 density is practically constant. Column (4) shows the same thing, *i.e.*, per unit weight of carbon the capacity of all fully activated chars is approximately constant, if the densities are less than the critical density. In this particular series, the cocoanut sample is somewhat above the critical density which accounts for its slight deviation from the constant in column (3).

On the other hand all cocoanut chars in which the selective oxidation has been substantially completed, but which are above 0.41 in apparent density, were found to obey the following empirical formula:

$$K = \frac{BP}{(1 - P) \times S} \qquad (1)$$

where $BP$ = porosity of the carbon granules, $P$ = total porosity and $S$ = service capacity. In other words the service (expressed either in minutes of service time or in weight of chlorpicrin adsorbed per c.c. of carbon) is a function of the porosity. The values of $K$ were experimentally determined from the following, which is another form of equation (1):

$$K = \frac{RD \times BP}{AD \times S} \qquad (2)$$

where $RD$ = real density and $AD$ = apparent density of 8–10-mesh carbon.

Table 2 gives data upon a series of steam-activated cocoanut charcoals from eight independent sources (samples of common

TABLE 2

| (1) Sample No. | (2) Series Letter | (3) $S'$[3] (Observed) Min. | (4) $BP$ | (5) $RD$ | (6) $AD$ | (7) $\frac{(RD \times BP)}{(AD)}$ | (8) $S$[4] | (9) $\frac{K}{K}K$ |
|---|---|---|---|---|---|---|---|---|
| Unactivated | | 0 | .253 | 1.56 | .715 | .51 | 0 | $\infty$ |
| 1 | *D* | 6 | .382 | 1.66 | .626 | .98 | .0027 | 370.0 |
| 2 | *E* | 112 | .350 | 1.63 | .634 | .90 | .0381 | 23.7 |
| 3 | *F* | 250 | .417 | 1.66 | .580 | 1.19 | .0832 | 14.3 |
| 4 | *D* | 387 | .532 | 1.87 | .525 | 1.90 | .1305 | 14.5 |
| 5 | *E* | 430 | .510 | 1.86 | .548 | 1.62 | .1449 | 11.3 |
| 6 | *C* | 464 | .504 | 1.98 | .590 | 1.69 | .1565 | 10.8 |
| 7 | *H* | 515 | .511 | 1.93 | .567 | 1.74 | .1740 | 10.0 |
| 8 | *E* | 525 | .510 | 1.90 | .563 | 1.71 | .1760 | 9.7 |
| 9 | *B* | 532 | .522 | 2.04 | .585 | 1.82 | .1805 | 10.1 |
| 10 | *E* | 540 | .537 | 1.96 | .544 | 1.93 | .1818 | 10.6 |
| 11 | *D* | 545 | .525 | 1.95 | .555 | 1.85 | .1830 | 10.1 |
| 12 | *D* | 566 | .537 | 1.90 | .529 | 1.93 | .1905 | 10.1 |
| 13 | *E* | 577 | .600 | 2.02 | .497 | 2.38 | .1943 | (12.7) |
| 14 | *C* | 580 | .535 | 2.04 | .572 | 1.90 | .1957 | 9.7 |
| 15 | *B* | 600 | .540 | 2.08 | .576 | 1.94 | .2020 | 9.7 |
| 16 | *C* | 605 | .505 | 2.02 | .600 | 1.70 | .2040 | (8.3) |
| 17 | *A* | 610 | .545 | 2.04 | .558 | 2.00 | .2060 | 9.7 |
| 18 | *B* | 615 | .574 | 2.10 | .539 | 2.23 | .2077 | 10.7 |
| 19 | *B* | 654 | .584 | 2.08 | .521 | 2.31 | .2207 | 10.5 |
| 20 | *A* | 662 | .575 | 2.09 | .534 | 2.25 | .2240 | 10.0 |
| 21 | *H* | 687 | .515 | 2.03 | .591 | 1.77 | .2317 | (8.1) |
| 22 | *A* | 700 | .584 | 2.15 | .540 | 2.31 | .2354 | 9.9 |
| 23 | *H* | 760 | .545 | 2.02 | .553 | 1.98 | .2555 | (7.9) |
| 24 | *H* | 775 | .567 | 2.02 | .535 | 2.11 | .2615 | (8.0) |
| 25 | *C* | 800 | .584 | 2.08 | .522 | 2.31 | .2680 | (8.7) |
| 26 | *F* | 805 | .617 | 2.11 | .484 | 2.70 | .2713 | 9.9 |
| 27 | *F* | 825 | .617 | 2.11 | .484 | 2.70 | .2780 | 9.7 |
| 28 | *F* | 845 | .612 | 2.11 | .488 | 2.65 | .2855 | 9.3 |
| 29 | *F* | 900 | .654 | 2.17 | .452 | 3.13 | .3033 | 10.2 |
| 30 | *H* | 955 | .665 | 2.14 | .432 | 3.28 | .3207 | 10.2 |

source are indicated by the same series letter between which the degree of oxidation is the only variable). These samples are arranged in the order of their service capacity shown in column (3). A well-defined break appears with increasing activity at a service capacity of about 450 minutes. The initial activation period is marked by rapidly falling values of $K$. The second stage, covering a service range of from 450 to 950 minutes or a chlorpicrin capacity of from 0.16 to 0.32 grams per c.c. of carbon, exhibits a well-defined tendency for $K$ to approach a constant value. Considering the

[3] $S'$ = number of minutes Standard C. W. S. Test.

[4] $S$ = grams of chlorpicrin absorbed per 1. c.c. of charcoal.

necessarily approximate nature of the experimental values, and the extraneous variables in the preparation of the carbon samples, the agreement in the values of $K$ is unmistakably significant. This table reveals two of the three characteristic stages occurring in the progressive activation of carbon by oxidation:

*First*, the stage of "selective" or "differential" oxidation in which the *chemical* character of the carbon is undergoing rapid change by the elimination of associated hydrocarbons. In this stage the adsorptive power increases at a rate out of all proportion to the increase in porosity as shown by the rapidly falling value of $K$.

*Second*, the stage of "limited" oxidation which commences after the chemical changes on the exposed carbon surfaces have been substantially completed. That the sole function of this continued oxidation is to increase the porosity and available surface is shown by the fact that $K$ becomes constant and therefore that the increase in capacity is derived principally from physical changes in the carbon which are mathematically expressible as a function of its porosity. In the latter part of Table 2 this second stage is shown approaching the limit set by the critical density of 0.4. Unfortunately the third stage is not represented as the samples selected for this series did not happen to pass through the critical density, but Table 1 serves the same purpose, showing the final phase below the critical density where the capacity per unit mass displays a constant value over a four-fold range in densities.

Further direct evidence confirming the existence of these three characteristic phases of selective and limited oxidation has been presented by one of the authors recently (33) in which it was shown that the first stage of activation is characterized by a very rapid decrease in hydrogen content corresponding with the selective removal of the hydrocarbons. In the period of limited oxidation following, the hydrogen content becomes practically constant, and the retentivity at first continues to increase with increasing porosity corresponding with the second stage and finally becomes constant as the third stage is reached.

The best gas-adsorbent carbon can never be made directly from wood charcoals. With the exception of a few hard woods of which the supply is negligible, the wood chars are too low in density even before activation. Only by pulverizing low density wood charcoals and briquetting them to denser chars can they be made to compare with dense nut chars. On the other hand, cocoanut shell chars as

obtained immediately after distillation are too high in density. Therefore after the "differential" oxidation is substantially completed, the oxidation process must be continued through a definite secondary stage, until the critical apparent density is reached, if the maximum adsorptive capacity is to be attained.

In commercial practice the rapidly mounting costs of continued oxidation sometimes make it advisable to stop short of the ideal or theoretical density for certain industrial uses. In other cases high capacity is so vitally important to the efficiency of the process that the higher cost of the carbon becomes a secondary matter. This is also true of carbon for military purposes. The engineer must determine in each case to what extent space and high capacity per unit of volume is a vital factor and be prepared to pay the necessary premium for his requirements.

## Theory of Alpha and Beta Modifications

Now turning back for a moment to the postulates of the original theory, discussion of these since their publication has centered principally around the statement that the active and inactive forms of carbon constituted two distinct "modifications." It is of course possible to argue endlessly over matters of definition. The term "modification" was purposely selected as sufficiently broad to permit more exact definition on further evidence. To quote the language of the paper: "It would be premature to assert that these two forms of carbon are true allotropic modifications. It is not yet established that both forms are amorphous. . . . This much is established, the two forms are characteristically distinct and easily differentiated both by their properties and conditions of formation." However, in provisionally suggesting the terms *alpha* and *beta* carbon, for the active and inactive forms, expression was given to a belief that future work would disclose some tangible differences in molecular aggregation or arrangement corresponding to the unique difference in properties. It was considered extremely probable that *alpha* carbon would prove to be almost if not completely amorphous and of a loose, open structure—possibly having a large proportion of free valences by reason of this loosely packed arrangement; whereas *beta* carbon was expected to prove more akin to graphite, having a more definitely close-packed or crystalline structure. In our laboratories the latter was sometimes referred to as "amorphous graphite." In view of this it is interesting to note that Professor

Briggs of Edinburgh, after taking exception to our classification, proceeds to ascribe the difference between the active and inactive forms to a difference in the degree of "polymerization" (2).

In view of the widespread interest and speculation on this subject we are perhaps warranted in pointing out the trend of our present investigations, and in indicating the nature of certain tentative conclusions which we have drawn therefrom. While these conclusions are now being subjected to a rigorous examination before being put out in final form, they serve to indicate the basis upon which we hope to obtain a final answer as to the existence and nature of the structural differences between *alpha* and *beta* carbon, as defined by the terms "active" carbon and "inactive" carbon.

Briefly stated, the X-ray crystallographic and chemical evidence thus far obtained indicates that all forms of carbon (the diamond excepted) fall into two main classes, the "graphitic" and the "pseudo-graphitic."

All normal graphites, natural and artificial, are sharply crystalline[5] and have a common characteristic X-ray pattern. They all yield graphitic acid by the Brodie reaction.

The pseudo-graphites are also definitely crystalline, but have a distinctly modified X-ray pattern, and apparently do not as readily yield graphitic acid. The proportions of these in mixtures can be identified by the X-ray to within 5 or 10 per cent. The pseudo-graphites also have an electrical resistance about 5 to 10 times higher than the graphites, the comparisons being based upon finely divided samples of each.

All other forms of carbon are converted into one of these two ultimate crystalline forms when heated above "graphitizing" temperatures. The types of free carbon from which active carbon is most easily derived, namely, carbohydrate and cellulosic chars, wood and nut charcoals, lampblacks, carbon blacks, etc., yield pseudo-graphite. Therefore in accordance with our previous nomenclature we have termed all the less highly polymerized forms of carbon which yield pseudo-graphite on heating, *alpha carbon*.

[5] All of the so-called "amorphous" graphites are completely crystalline; so also is graphitic acid which has a perfectly definite physical and chemical structure. The confusion caused by the close resemblances of these two forms of carbon is responsible for the thesis so elaborately developed by Kohlschutter (3) that graphite is not a definite chemical individual.

Correspondingly we may designate as *beta carbon* all forms of carbon which yield normal graphite on heating.

In the 1919 paper we defined the inactivatable forms of carbon, i.e., carbons set free from their compounds at high temperatures, as *beta* carbon. These forms now satisfy the new *beta* carbon classification by yielding normal graphite on heating.

On this basis active carbon appears to be simply a pure form of *alpha* carbon possessing fundamentally the elements of the pseudo-graphitic crystalline structure, whereas inactive carbon is *beta* carbon belonging to the graphitic type of structure. This apparently simple relationship is clouded somewhat by the fact that certain low temperature cokes and the coals yield beta carbon predominantly on heating and yet, as we have shown, are capable of reasonable activation. Either we must abandon the thesis that unique adsorptive properties are inherent in the special structure of *alpha* carbon, and conclude that both *alpha* and *beta* forms may be active if in a sufficiently degraded state of polymerization, or we must conclude that the coals and pitch cokes referred to above contain a certain percentage of *alpha* carbon, mixed with *beta* carbon. One possibility is that the free carbon in coal is largely *alpha* and that the *beta* carbon is formed in ordinary calcining from the large proportion of hydrocarbon residues in it having a high temperature of decomposition. In this case we should expect a *previously activated* anthracite coal to yield pseudo-graphite predominantly, because the hydrocarbons ordinarily giving rise to *beta* carbon on heating would have been chemically removed by oxidation. Our experimental work along these lines is not yet sufficiently advanced to say whether coals already contain *beta* carbon in considerable quantity or whether it appears later in the calcining stages.

However, other evidences of the relationships between the four forms of carbon, *alpha*, *beta*, *pseudo-graphite* and *normal graphite*, lead us to suspect that the special adsorptive powers of active carbon will be found to be unique to the *alpha* form.

Working in this Laboratory, Dr. W. B. Dexter, starting with normal graphite, has prepared graphitic acid, reduced the latter to a finely divided form of carbon by mild reducing agents, and reconverted this carbon to normal graphite by electric baking at the usual temperatures. By more violent methods of decomposition he has prepared small quantities of another form of carbon from the same graphitic acid, which upon heating appears to yield pseudo-

graphite. Since the transformations from graphite to graphitic acid and from the latter to the two forms of carbon take place directly in the solid phase, they are peculiarly instructive. Thus the evidence indicates that by a partial breaking down of the structure of the graphite crystal we obtain *beta* carbon which goes back to graphite on heating. If, however, we disintegrate the graphite crystal more completely, we obtain *alpha* carbon which then goes to *pseudo-graphite* on heating. This suggests that there is some element of complexity in the *beta* carbon grouping which determines its crystallization in the graphitic rather than the pseudo-graphitic form and consequently that *beta* carbon is probably more complex than *alpha* carbon.

We find further that *beta* carbon is in fact merely *colloidal graphite* and may be directly obtained by mechanically breaking down the graphite crystals to fragments of colloidal dimensions. This actually occurs in the preparation of Acheson Aquadag, which the X-ray shows to be highly polymerized *beta carbon* and which is made from fully crystalline graphite by a process of grinding and deflocculation. Colloidal graphite, such as Aquadag, exhibits no extraordinary adsorptive powers beyond those characteristic of all materials in so minute a state of subdivision. So far as we know neither it nor similar forms can be activated. It therefore seems reasonable to assume that the special adsorptive properties of active carbon are peculiar to the simpler structure of *alpha* carbon.

The transition from *alpha* carbon to pseudo-graphite with increasing temperature can be observed by the changes in X-ray patterns in exactly the same manner as the transition of *beta* carbon to graphite. This crystallization causes the *alpha* carbon to lose its special activity. Pseudo-graphite even when made from highly active carbon is not appreciably more active than graphite.

If the observations and relationships just indicated are substantiated by our subsequent work, the nature of the active and inactive modifications of carbon will be definitely established along the lines suggested in our original paper.

## II. Fundamental Criteria of Activation and of Adsorptive Capacity

This discussion relates to a phase of the commercial utilization of adsorptive materials of great importance, namely, the question of quantitative criteria of useful adsorptive capacity. To make real

headway it must be possible to market a standardized product permitting of definite engineering specifications.

The first essential step is a method of defining and measuring adsorptive capacity in terms which are of quantitative significance to the user, and at the same time are sufficiently simple and accurate for manufacturing control. The first such criteria to come into general use in this country were the "tube tests" developed and used by the Chemical Warfare Service as specifications for gas mask carbon (4).

Air containing a known concentration of toxic vapor, such as chlorpicrin, was passed at a constant rate into a tube of fixed diameter, containing a 10-cm. layer of carbon of a definite fineness. The capacity of the carbon was then expressed by the number of "minutes" to the "break point," i.e., to the point where a detectable trace of vapor appeared in the effluent air. The weight of gas adsorbed at the break point was also determined directly. For reasons which will be apparent, the "break point" on such a test is affected by many factors which bear no relation to the intrinsic character of the carbon itself, as, for example, the concentrations of the vapor, the rate of flow of the air, the fineness or mesh limits of the carbon, etc.

As the quality of the adsorbent carbon was improved, it became necessary to "accelerate" the tube tests by using higher concentrations and faster rates of flow. While such accelerated tests served to give relative values for manufacturing control at any given plant, they gave badly distorted values when applied to adsorbent carbons of different origin and type such as the American and German carbons. Therefore, not even for military uses were the accelerated tests authoritative.

Attempts were made to substitute a "saturation" test in which the absorbed gas was weighed after the carbon had come to equilibrium with a definite concentration of the gas at a definite temperature. In a C. W. S. report in 1919, one of the authors showed that in general a constant difference existed between the weight of gas taken up by the carbon on any given "saturation" test and the corresponding "tube test." This was explained as follows: The "break point" on the tube test corresponds to the point where the *rate* of adsorption falls below the rate at which the gas was being passed through the tube. This critical point appears to be reached when the residual unsaturated capacity of the carbon drops to a

constant minimum value, this constant value depending upon the particular factors of the tube test. Thus the two tests are not directly proportional, but the saturation values are proportional to the sum of the tube test values plus a constant, which is characteristic of the test. The "saturation test," while free of certain extraneous factors such as geometrical shape of container, gas velocity, etc., is extremely sensitive to gas concentration, and fails to show more than partial correspondence with the significant differences in behavior of various kinds of carbon, either for military or industrial purposes.

The reasons for this lack of correspondence lie in the dual character of the sorptive phenomena exhibited by carbon, as cited in the earlier paper (1). In his series of C. W. S. reports, Chaney showed that if pure air were passed over the carbon, either after the break point on the tube test, or after the saturation test, the losses of absorbed gas were first very high and then fell to a gradual and almost negligibly low rate—one too slight to be detectible by the usual methods of determining the "break point." Plotted logarithmically, the periods of rapid and slow weight loss appeared as two intersecting straight lines, indicating a more or less abrupt discontinuity between the two rates of loss. The weight of adsorbed gas corresponding to the period of extremely slow weight loss was termed the "retentivity" of the carbon. The retentivity values for a series of typical carbons were found to bear no fixed relationship whatsoever to the "saturation" values, but to show a most significant correspondence to certain other properties of the carbons, such as their value for vapor recovery from low concentrations, their power to adsorb substances in true solution, such as iodine, and their relative value for different kinds of toxic gas removal. The conclusions were drawn that the retentivity values corresponded most nearly with what was termed the "specific" adsorptive capacity, i.e., associated with the chemical properties of the active carbon, and that the excess of more easily removable gas or vapor was held by capillary forces associated with the physical or microscopic structure of the carbon. A further reason for believing that the "specific" adsorptive power represented specific polar forces was the observation that water, for example, showed a zero retentivity value, being practically completely removed by the passage of dry air at room temperature. The high retentivity values for hydrocarbon derivatives were thus directly associated with the chemical

nature of the adsorbed vapors, and not merely with their physical properties, such as the boiling points. The industrial significance of this will be discussed later in connection with comparative data on silica gel.

The method of determining the retentivity by passing air over the saturated carbon at room temperatures was one requiring several hundred hours for completion, and consequently means of accelerating the test were sought. As finally developed to a routine procedure in this laboratory the method consists in first saturating the dried and evacuated carbon with toluene at 22° C., the weight of absorbed gas after equilibrium is established, giving the "saturation value." The carbon is then evacuated to 2 mm. of Hg at 100° C., weighings being taken each half hour. When the last three weighings lie on a straight line, the intercept of this line extended to the $y$-axis is taken as the retentivity value. Fig. 1 illustrates the type of curves obtained in hundreds of determinations. The difference between the saturation value and the retentivity value we have called the "capillary" value of the carbon. The ratio of capillary and retentivity values may vary enormously, and

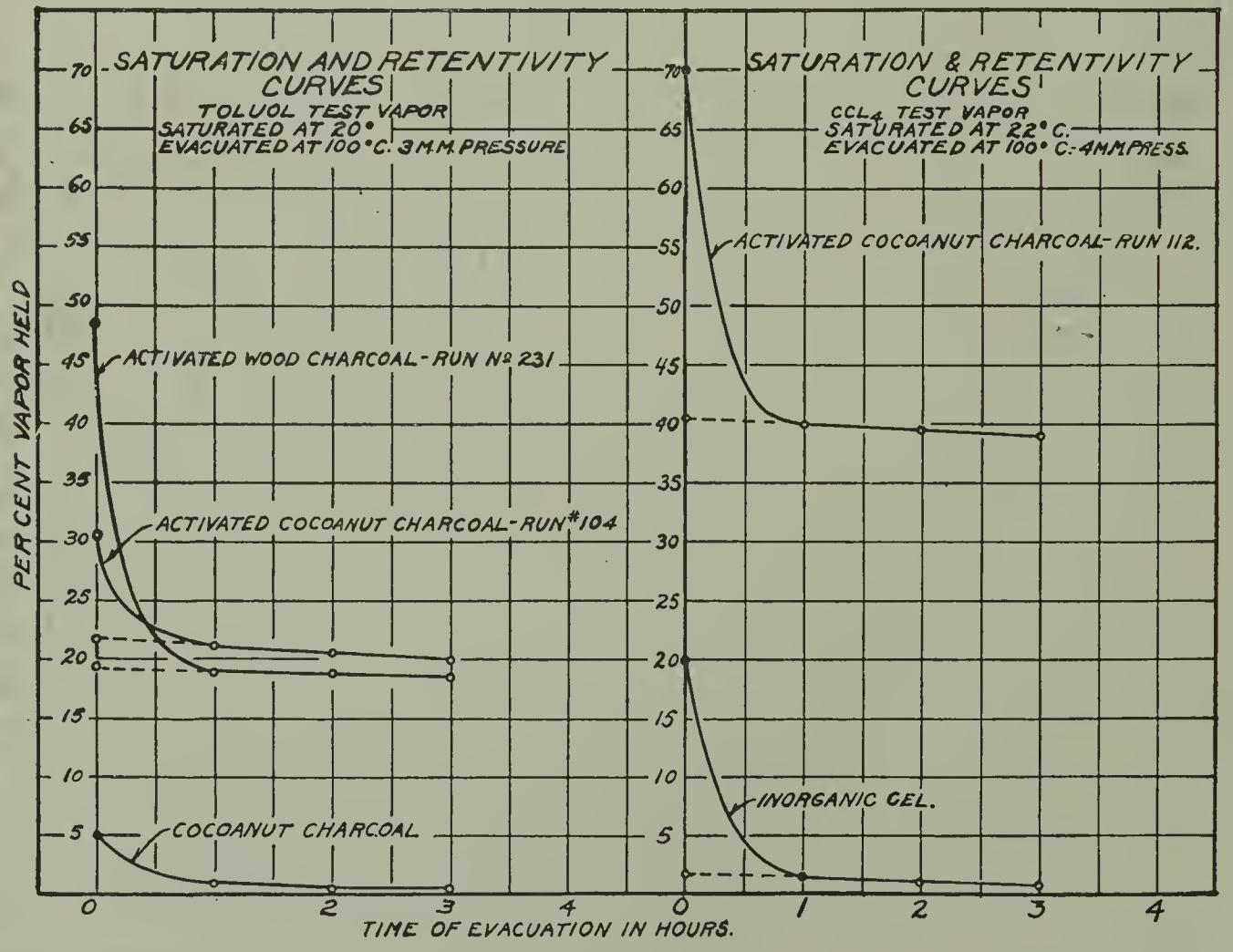
SATURATION AND RETENTIVITY CURVES
TOLUOL TEST VAPOR
SATURATED AT 20°
EVACUATED AT 100°C. 3 M.M. PRESSURE
ACTIVATED WOOD CHARCOAL - RUN Nº 231
ACTIVATED COCOANUT CHARCOAL - RUN #104
COCOANUT CHARCOAL
SATURATION & RETENTIVITY CURVES
CCL4 TEST VAPOR
SATURATED AT 22° C.
EVACUATED AT 100° C. - 4 M.M. PRESS.
ACTIVATED COCOANUT CHARCOAL - RUN 112.
INORGANIC GEL.
PER CENT VAPOR HELD
TIME OF EVACUATION IN HOURS.

FIG. 1.

therefore the saturation and retentivity curve serves to define the sorptive characteristics of any carbon with a definiteness and completeness unapproached by any other method.

It is true that the retentivity values thus obtained are also purely relative, the absolute weights of retained gas depending upon the chemical nature of the vapor selected, the temperature at which it is removed, and upon the degree of vacuum employed. On the other hand, the values thus obtained are the first to show any broad relationships and permit of any basic generalizations as to various types of adsorptive phenomena, and hence must be accepted as cor-

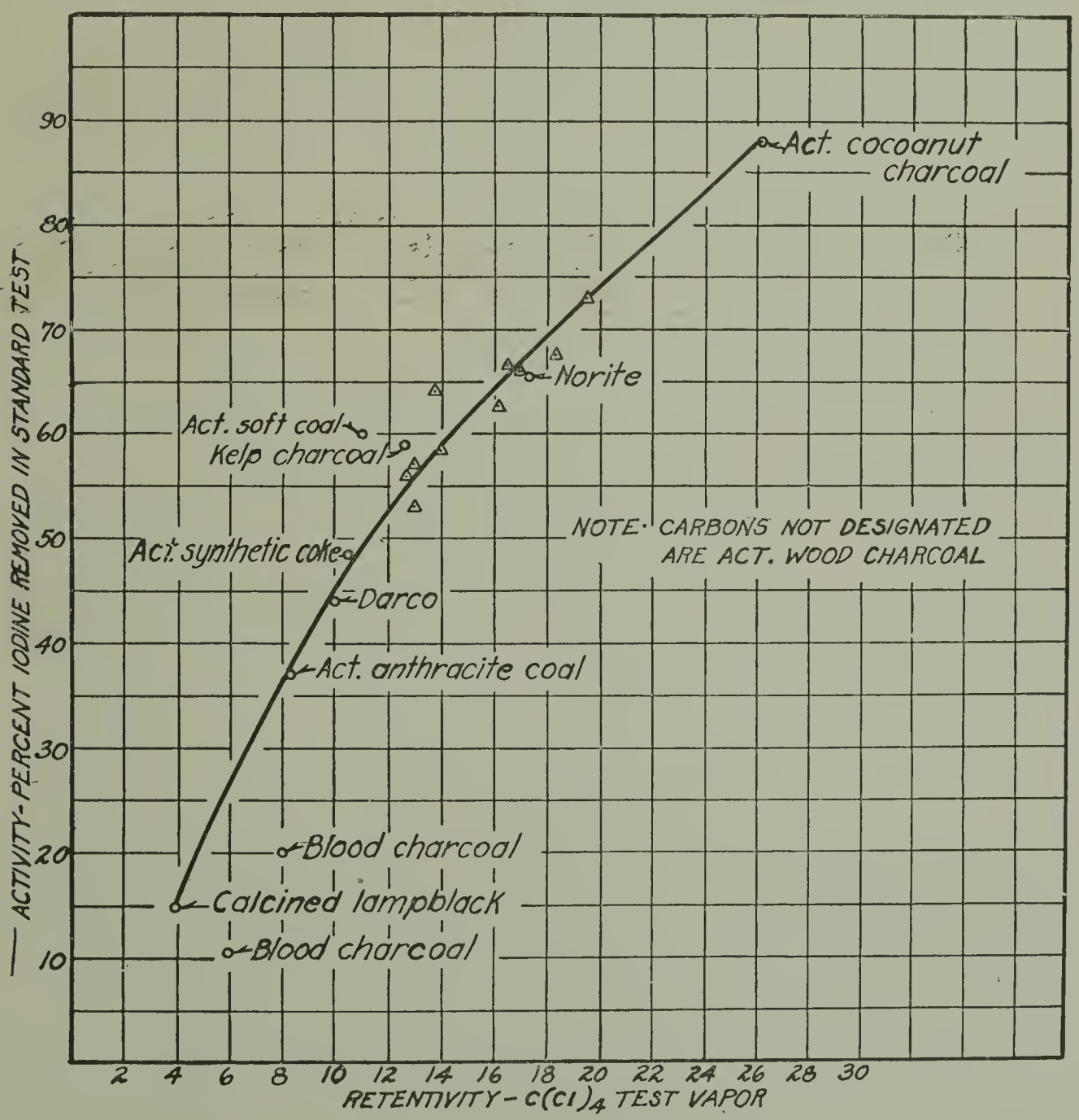


FIG. 2. Relationship between "activity" and "retentivity" of various types of activated carbons. All carbons acid-extracted, thoroughly washed and dried before testing.

responding in some real way to a fundamental property of the carbon. The exactness of this correspondence with the "iodine adsorption number" of the carbon, for example (see Fig. 2), has permitted the substitution of the latter and simpler test whenever the retentivity value alone is required, as is usually the case for carbons of known type where the ratio of capillarity to retentivity has been previously determined. It is also evident that when this ratio is known for a given type of commercial carbon, the "saturation" values alone can be used as a commercial test, without serious error. To compare or define an unknown carbon, however, the complete determination is necessary both of the saturation value and of either the retentivity or the iodine number. The latter value we have termed the "activity" of the carbon, and is obtained by determining the amount of iodine which 1 gram of dried, 200-mesh carbon will absorb from 50 c.c. of 0.2 N iodine-potassium iodide solution. The mixture is agitated for 3 minutes, filtered and the first runnings discarded. The iodine concentration of an aliquot portion of the filtrate is determined by titration. Highly active carbons will remove around 90 per cent of the iodine.

Other criteria of carbon activation have been proposed, notably the method of Dr. Lemon (5) who has measured the relative vacuum produced by the adsorption of air or nitrogen at liquid air temperatures. The pressure curves thus obtained in Fig. 3 are related to the retentivity or, as Professor Briggs (6) defines it, the "prehensility" of the carbon, but both the technical difficulties of the method and the greater difficulty of expressing the values in convenient quantitative terms make it of theoretical interest only.

## III. General Processes of Carbon Activation, Comparatively Summarized.

The previous discussion has shown that according to our theory any process of releasing carbon from its compounds at sufficiently low temperatures in the absence of hydrocarbons or other strongly adsorbed substances should yield highly active carbon directly.

This has been accomplished in several ways: for example, by employing the reaction $2CO = C + CO_2$ which can be brought about at 300° C. in the presence of an iron oxide catalyst (this reaction was first suggested in the present connection by Patterson at the American University in 1918), and by the action of sodium (7) or mercury (8) on carbon tetrachloride. Such methods are of

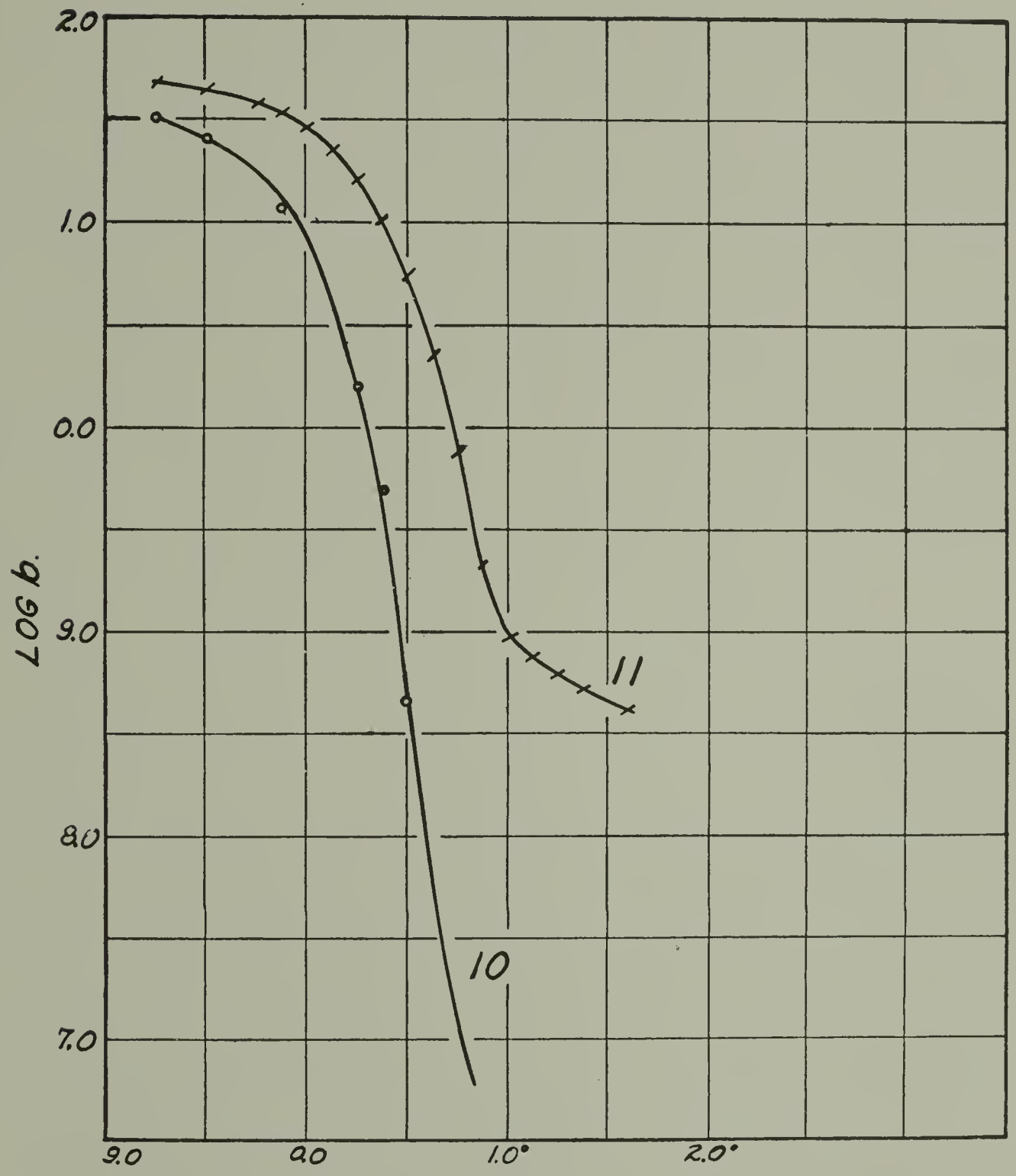


FIG. 3.

purely theoretical interest, as the resulting carbon lacks the necessary mechanical properties for use even as a decolorizing carbon, as will be more fully discussed in a later section.

The requisite physical structure for commercial uses can be obtained only in suitably prepared chars, cokes or coals which we have termed "primary carbon." These all require "activation," that is, the adsorption complex characteristic of the primary carbon must be broken up and the hydrocarbon constituents eliminated. The following methods have been employed or suggested.

### 1. *High Temperature Calcination*

The difficulties of this on a commercial scale are evident from the theory.

The stabilization of the hydrocarbons by adsorption usually raises their final decomposition temperature above the critical temperature range and inactive carbon is formed. By selecting chars naturally having a low decomposition point and conducting the operations with great care a limited degree of activation can be effected. However, the method does not permit any control of the resulting porosity of the carbon granules, and is only effective on chars of very low density which means low structural strength, and low capacity per unit volume of adsorbent. The wood charcoals employed for gas masks by the British and French were chiefly prepared by this method.

### 2. *Carbonization with Mineral Additions*

The carbonaceous materials may be impregnated with a variety of metallic salts or oxides before carbonization. These seem to be effective in preventing the formation of the adsorption complex of hydrocarbons or in causing the decomposition of the adsorbed hydrocarbons. This removal of mineral matter provides an exceedingly porous structure with capillary pockets of molecular dimensions. Such carbons possess a relatively high capillary capacity, but exhibit the specific adsorptive characteristics of active carbon only to a limited degree. The German gas mask carbon was prepared by this method, the wood being impregnated with zinc chloride, calcined and then the zinc dissolved out by hydrochloric acid. This type of process is familiar in the commoner methods of preparing certain decolorizing carbons. Sometimes the mineral naturally occurs in the vegetable fiber as in the case of "Carbrox" made from rice hulls.

### 3. *The Use of Solvents*

It has been proposed to dissolve the hydrocarbons out of the primary carbon by special solvents, such as selenium oxy-chloride (9). Such methods, apart from their expense, do not appear commercial even for war emergencies, as they do not afford means of controlling the porosity or density of the final product. The problem of getting rid of the solvent is also a serious one.

### 4. *Processes Involving the Principles of "Differential" and "Limited" Oxidation*

Of universal applicability to all primary carbons and of the widest flexibility, both as to the manner of employment and as to the variety and quality of the resulting product, are the processes involving what we have termed "differential" and "limited" oxidation. While these may be carried out by either wet or dry methods, in their preferred forms the oxidizing agents are gases, such as air, steam, $CO_2$, chlorine, etc. The principle of such selective chemical attack depends upon the slightly greater susceptibility to oxidation of the hydrocarbon constituents of the adsorption complex than of the active carbon itself. By a proper adjustment of the oxidizing environment, as to temperature and concentration, the adsorbed hydrocarbons may be eliminated from the active carbon far more effectively and economically than by any other processes hitherto employed, and in the same environment the formation of inactive carbon may be reduced to a minimum. The Chemical Warfare Service employed both air and steam activation on a large scale. The product obtained by air is inherently inferior to the best steam-activated products, chiefly because the difficulty of nicely controlling the temperature and rate of an exothermic reaction is much greater than is the control of an endothermic one. Too harsh an oxidizing attack destroys both active carbon and hydrocarbons simultaneously, consequently nothing is accomplished by it except a general increase in porosity.

The quality of activated carbon therefore depends upon the skill with which the manufacturer is able to control the oxidation environment as well as upon the preliminary preparation of the char.

The essential features of the steam-activating processes were worked out by an Austrian, Ostrejko, a year or more prior to the American disclosures. For military reasons his patents were withheld from issue in Austria until after the war, although curiously enough he obtained an issue from the British Patent Office in the spring of 1918 (10). His disclosures, therefore, were unknown to the allied chemists until after the American processes were in operation, and were apparently not developed and employed by either Austria or Germany during the war.

## IV. Adsorption of Gases and Vapors: Dissimilarity of Carbon and Silica Gel

The three essential characteristics of a gas-adsorbent carbon are good mechanical strength, a close approximation to a definite optimum density or porosity, and high intrinsic "activity."

The necessity for mechanical strength to avoid crushing, packing and dusting in containers or towers through which large volumes of gas must be passed at high velocities is obvious.

The fact that the efficiency both of military and industrial gas-adsorbing vessels is rated upon the size of the container, rather than upon the weight of the adsorbent filler, automatically determines the ideal porosity of the adsorbent in the manner discussed in Section I.

Section II has also shown why the most significant criterion of the adsorptive capacity of carbon is its "specific capacity" as defined by the "retentivity" for certain adsorbed gases, or by the equivalent values of the iodine adsorption from solution, designated as the "activity." The industrial significance of the "activity" values will be further developed in connection with the question of "preferential" or "selective" sorption, a quality of solid adsorbents which is made strikingly apparent by the "retentivity" method. In respect to this property, we find active carbon and silica gel diametrically opposed with respect to their relative adsorption of water and hydrocarbon derivatives.

We have already referred to the fact that if the "retentivity" of carbon were defined by its power of retaining water vapor, instead of toluol, for example, the retentivity would be zero. In a stream of dry air, carbon gives up its water at room temperatures. Applying the same criteria to silica gel, we find that its "specific" adsorptive power, while much less marked than that of carbon, is definitely selective for water. In fact, all of the water cannot be expelled from the gel without breaking down the physical structure of the granules, and this makes the selection of a basis for defining the water retentivity a little difficult. If, however, the gel, dried at 200°C. (and already containing about 3 per cent of water), is saturated with water and the additional water retained at 100° C. is determined, this is found to be about 2.5 per cent, whereas the toluol retentivity of the gel treated in the same manner is but 1.5 per cent. That is, the ratio is 5 to 3 in favor of the water. If the original water content is included, the ratio of water to toluol is 4 to 1.

That this selectivity of adsorption is a very practical reality is readily demonstrated by the simple experiment of shaking up a mixture of water and benzol with activated carbon and with silica gel respectively. The carbon will adsorb the benzol, and if enough benzol is present to saturate the carbon, the water will be completely rejected. The silica gel will take up the water and reject the benzol. These facts prove beyond question that any theory of adsorption which disregards the chemical nature of the adsorbent and adsorbed substances is incomplete from a theoretical point of view and inadequate from a practical standpoint. As a matter of fact, even a "capillary" theory of adsorption must recognize the predetermining influence of specific chemical factors, inasmuch as capillary phenomena may exhibit certain sharply contrasting aspects depending upon whether the capillaries are "wet" by the liquid or not. Such differences in the "wetting" action reveal the operation of specific chemical or polar forces, which are not explicable on any mathematical concept as simple as relative capillary diameters (32). This is said not to minimize the significance of the rôle played by capillary structure in the dispersion of solid adsorbents, nor to deny the value of statistical studies of capillary and pore volumes in the case of any given adsorbent, but to avoid a fictitiously simple classification of all adsorbents and adsorptive phenomena on the basis of mechanical structure.

In Table 3 are characteristic data on the sorptive capacities of typical samples of activated carbon, silica gel, and sil-o-cel, both

TABLE 3

SORPTIVE CAPACITY OF ACTIVATED CARBONS AND SILICA GEL

Saturation in pure vapor at 25° C.
Retentivity at 100° C. and 3 mm. Hg pressure.

| Substance. | Apparent Density | | Sorptive Capacity Expressed as Grams $CCl_4$ held by 100 Grams of Sorbent | |
|---|---|---|---|---|
| | 8–14 Mesh | Total | Capillary | Specific |
| Activated Carbon—*A* | 0.465 | 110.9 | 80.9 | 30.0 |
| " " —*B* | 0.500 | 103.8 | 75.3 | 28.5 |
| " " —*C* | 0.542 | 95.7 | 68.7 | 27.0 |
| " " —*D* | 0.560 | 79.5 | 51.5 | 28.0 |
| Silica Gel—*A* | 0.720 | 19.8 | 17.8 | 2.0 |
| " " —*B* | 0.700 | 39.2 | 37.7 | 1.5 |
| Sil-O-Cel | | 12.3 | 10.3 | 2.0 |

their specific capacities or retentivities under similar conditions, and their total saturation capacities. Attention is first called to the fact that the sorption by silica gel and sil-o-cel for carbon tetrachlorid, for example, is almost wholly of the "capillary" type, their "retentivity" for this class of substances being practically negligible, under the conditions of the test. The industrial significance of these differences in retentive power is shown by Fig. 4, dealing

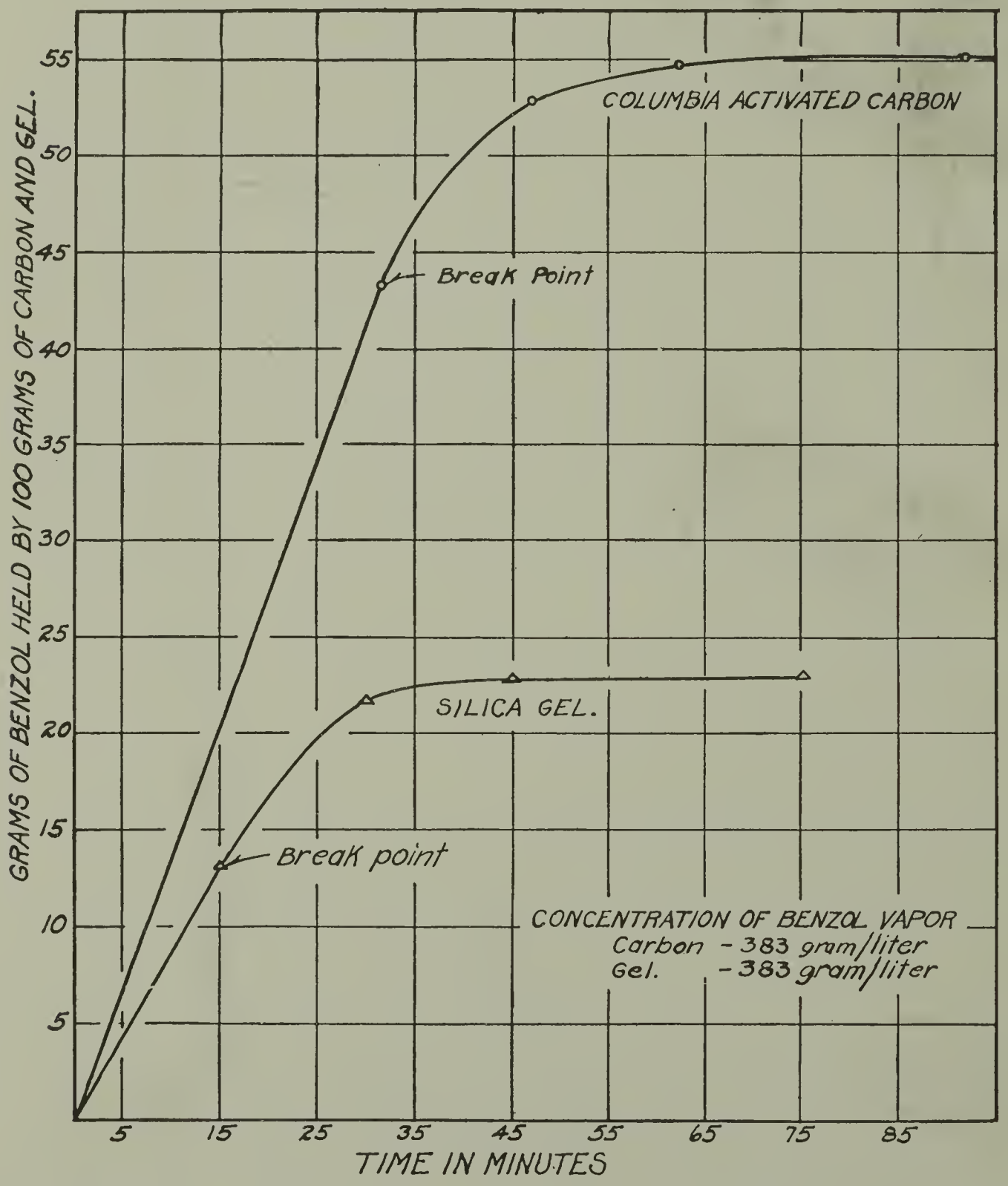


FIG. 4. Sorption of benzol vapor from dry air by activated carbon and silica gel. Equal volumes (30 c.c.s.) of 8–14 mesh carbon and gel compared. Air-benzol mixture passed at rate of 500 ccs./min. Temperature 25° C.

with the relative recovery of benzol from *dry* air by carbon and silica gel respectively. The most significant points on these curves are the "break points" representing the end of the period of complete sorption of benzol. These results are typical of the superiority exhibited by activated carbon over silica gel for all organic vapors and solvents. The conditions above are those most favorable to the silica gel because the benzol-air mixture was moisture-free. The industrial significance of a solvent-preferring versus a water-preferring adsorbent is illustrated by the data in Table 4 showing the relative recoveries of benzol from *dry* and *moist* air respectively. The efficiency of the carbon is slightly impaired, but the silica gel becomes entirely valueless.

TABLE 4

PREFERENTIAL SORPTION OF BENZOL AND WATER VAPOR BY ACTIVATED CARBON AND SILICA GEL

| Sorbent | Wt. of Sorbent | Air | Breakpoint | | Saturation | | Conc. of Benzol. |
|---|---|---|---|---|---|---|---|
| | | | Time | % Benzol Held | Time | % Benzol Held | |
| Carbon, B | 33 grams | Dry | 230 min. | 27.8 | 420 min. | 34.9 | .0133 g. liter |
| " " | " " | " | 207 " | 31.9 | 420 " | 34.9 | .017 " " |
| Gel, B | 50 " | " | 62 " | 5.0 | 420 " | 12.0 | .0134 " " |
| " " | " " | " | 68 " | 5.6 | | | .0137 " " |
| Carbon, B | 33 " | Moist | 166 " | 21.2 | | | .0142 " " |
| " " | " " | " | 162 " | 20.9 | 420 " | 27.3 | .0142 " " |
| Gel, B | 50 " | " | 29 " | 2.4 | 420 " | 0.0 | .0135 " " |
| " " | " " | " | 28 " | 3.0 | 420 " | 0.0 | .0178 " " |

*Note.*—The amount of benzol adsorbed from moist air was determined by removing it from the sorbent by steam.

Equal volumes of 8–14-mesh carbon and gel B used.

Dry air containing benzol or air containing approximately equal parts by weight of water vapor and benzol passed at rate of 3000 ccs. min.

It is this selective adsorption of water which destroys the military value of silica gel, ferric oxide gel, and similar hydrophilic adsorbents, and the lack of it that makes carbon unique and irreplaceable.

### *The Removal of Volatile Substances from Carbon*

In certain quarters it has been argued that the high retentivity of carbon for the commoner volatile solvents and chemicals was not an advantage but a handicap in industrial recoveries because of the supposed difficulties of removing the adsorbed materials from the carbon.

As a matter of fact, for most substances which it is desired to recover, this difficulty does not exist. While the retentivity of carbon for many hydrocarbon derivatives is marked in comparison with that of other adsorbents, and while the relative retentivity value under arbitrarily selected conditions has been found to afford one of the most significant indexes of the characteristic sorption properties of carbon, nevertheless, the retentive power rapidly diminishes at critical temperatures characteristic for each substance, and the more volatile chemical vapors are removed from carbon as readily as from silica gel at moderate temperature elevations, especially when aided by steam distillation or vacuum. Comparative data are given in Table 5.

TABLE 5

REMOVAL OF SORBED VAPORS FROM ACTIVATED CARBON AND SILICA GEL BY HEATING AT 150° C.

Saturated materials exposed in a thin layer in a ventilated oven and heated for 1 hour at 150° C.

| Solvent | Percentage Solvent Held at Saturation by | | Percentage Solvent Retained at 150° C. | |
|---|---|---|---|---|
| | Carbon B | Gel B | Carbon | Gel |
| Methanol | 50.0 | 20.0 | 1.21 | 1.50 |
| Ethanol | 50.0 | 20.0 | 1.05 | 1.54 |
| Isopropanol | 50.0 | 20.0 | 1.15 | 1.75 |
| Ethyl Acetate | 57.5 | 25.0 | 4.87 | 2.84 |
| Acetone | 51.0 | 20.0 | 2.93 | 1.20 |
| Acetic Acid | 70.0 | 25.0 | 2.23 | .75 |

In the case of materials immiscible with water, steam or hot water provide the simplest and most rapid method of introducing the required heat. Moreover, the drying of the carbon after the removal of the adsorbed materials by steam or water is in many cases unnecessary, owing to the non-selective sorption of the latter, and its easy displacement by preferentially adsorbed vapors. This possible omission of the drying step constitutes a unique economic advantage in certain industrial sorption cycles employing carbon. Substances miscible in water require indirect heating or rectification.

### *Typical Commercial Applications of the Gas-Adsorbent Types of Activated Carbon*

There are five general fields in which the gas-adsorbent carbons have marked technical possibilities.

### (1) *Recovery of Gases, Solvents and Vapors in Dilute Concentrations*

(*a*) The recovery of gasoline from natural gas (11–12), the recovery of solvents such as petroleum ethers, benzol, sulphuric ether, amyl acetate, alcohol, etc., from the air (13).

The recovery of acetone, butanol, ethanol, etc., from water-laden gases passing out of fermenting vats (14); recovery of ethylene and removal of sulphur compounds (15), as well as benzol and light oil, from illuminating gas (16); recovery of oxides of nitrogen, $SO_2$, etc.

(*b*) The abatement of objectionable stenches and odors, e.g., from rendering plants and the like (17); the purification of air in submarines; the deodorizing of confined spaces in refrigerating rooms, etc.

(*c*) Military, firemen's and industrial protective masks (18).

### (2) *Purification of Gases*

(*a*) Refining of helium (19).

(*b*) Purification of gases, e.g., to make $CO_2$ from fermenting vats available for carbonated waters; purifying hydrogen and nickel carbonyl (20) for hydrogenation purposes; purifying ammonia (21) before its catalytic oxidation, etc.

### (3) *Catalysis of Gas Reactions*

(*a*) Decomposition or oxidation of $H_2S$ to yield free sulphur (15).

(*b*) Decomposition of phosphine (in ammonia and acetylene (22) purifications).

(*c*) The oxidation of nitric oxides (23) by air (500-fold accelerations have been obtained in comparison with ordinary tower processes).

(*d*) Chlorination of hydrocarbons (24); also of CO in the manufacture of phosgene.

(*e*) As a general means of facilitating reactions between a gas and a liquid by passing the two counter-currently through a column of granular carbon (25). Applicable in bleaching, in sterilizing water and other liquids with chlorine, in the oxidation of drying and semi-drying oils, in the decomposition or oxidation of mineral oils for conversion into fatty acids, etc. The usefulness of active carbon in catalytic reactions may be widely extended through its impregnation with various metals, oxides and salts.

### (4) *The Storage of Compressed Gases*

It has been shown that at corresponding pressures, more of certain fixed gases can be stored in a cylinder containing highly active carbon than in the same cylinder with no carbon present (26). This is due to partial liquefaction of the gases by adsorption at high pressures, and is exhibited only by adsorbents possessing a high retentivity.

### (5) *Evacuation of Vessels*

This is allied to (4) above, the production of high vacua being a function of the retentivity of the carbon. In these uses, carbon is again sharply differentiated from silica gel which has a low evacuating power or "prehensility."

The carbon may be used

(*a*) For cheaply and simply evacuating commercial heat insulating containers and

(*b*) In various forms of special apparatus where a sensitive method of regulating the vacuum or of maintaining it in the presence of slight gaseous decompositions is desired.

## V. Adsorption from Liquids and Solutions

### *Two Generalizations on the Adsorption of Substances from Liquids and Solutions by Carbon.*

An examination of the voluminous literature upon decolorization of sugar and other solutions by carbon suffices to indicate a considerable degree of confusion and incoherence in the technology of decolorizing carbons. Theoretical discussions of the inherent properties and behaviors of such carbons have notably failed to produce any broad generalizations which could adequately satisfy the known facts. In our study of decolorizing problems in this laboratory, Dr. Ray has employed to unique advantage the systematic variations in carbon activity and structure made possible by precise control of the activating processes, and has utilized the special methods of evaluating active carbon described in Section II preceding. He has found that the various phenomena relating to decolorizing and adsorptive efficiencies can be adequately correlated and the behavior of any decolorizing carbon fairly accurately predicted under diverse circumstances on the basis of two very simple generalizations which will be stated below.

*A*. The adsorptive power of any carbon for substances in liquids is directly proportional to its "activity" (as defined by the "retentive" capacity of the carbon for gases) provided the units of the substances to be adsorbed are small enough or the porosity or subdivision of the carbon is great enough to permit unobstructed access to the active carbon.

Two special cases exist.

(1) If the dispersion of the carbon (i.e., its porosity or fineness) passes certain limits, its adsorptive power becomes com-

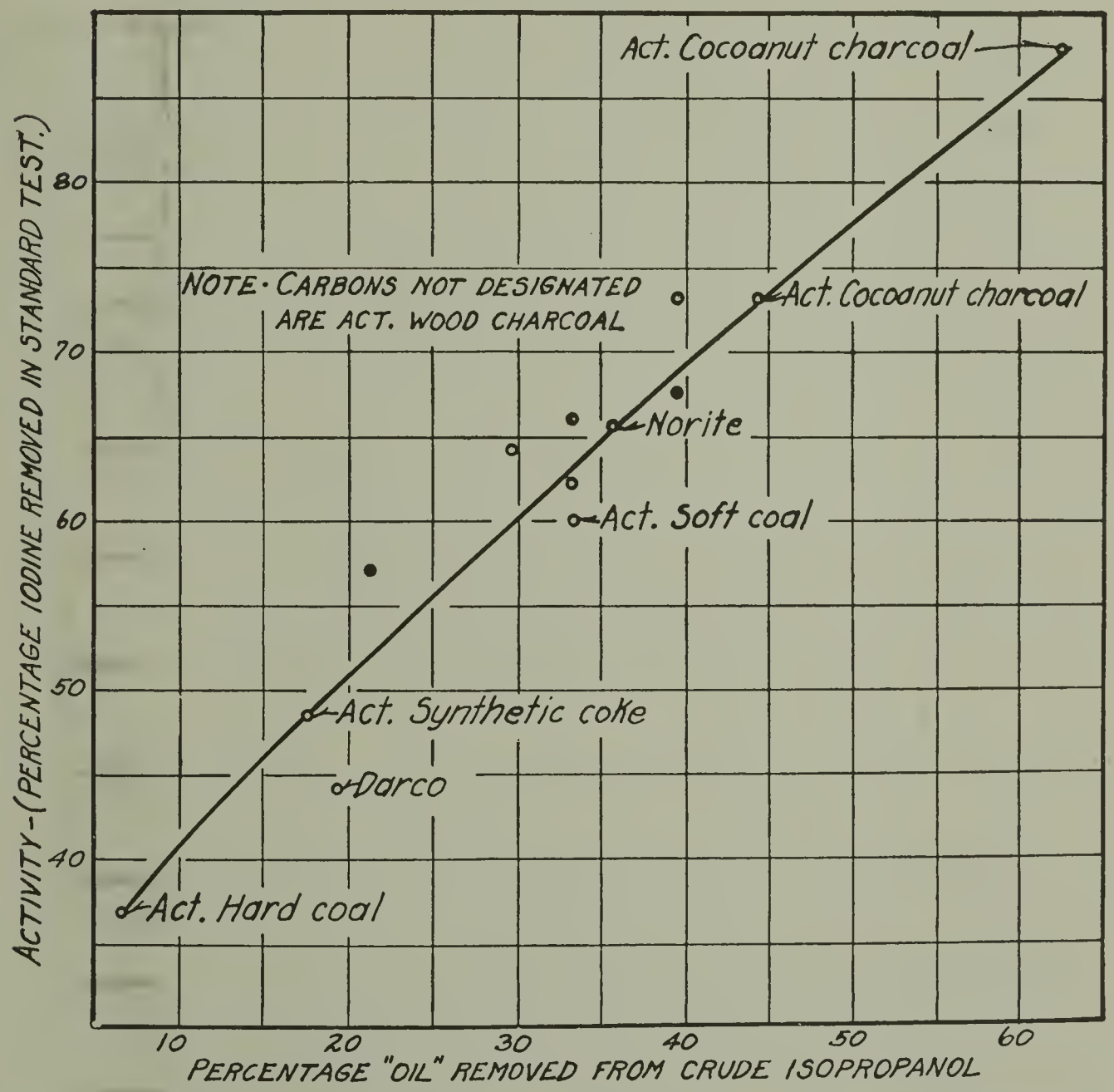


FIG. 5. Relationship between activity and alcohol-purifying power of various types of activated carbon. All carbons pulverized to pass 200-mesh screen, acid-extracted, thoroughly washed and dried before testing. Crude isopropanol containing objectionable oil treated with 5 per cent. carbon in the cold. Oil determination made by comparing turbidities on dilution by means of nephelometer.

pletely defined by its "activity," independently of the dimensions of the particles adsorbed.

(2) If the dispersion of a carbon is limited, its adsorptive power for larger particles of colloidal dimensions becomes a function not only of the activity of the carbon but also of its apparent density and of its fineness.

*B.* The adsorptive power of carbon for particles bearing an electrical charge is diminished if the carbon bears a charge of like sign and increased if the carbon is oppositely charged.

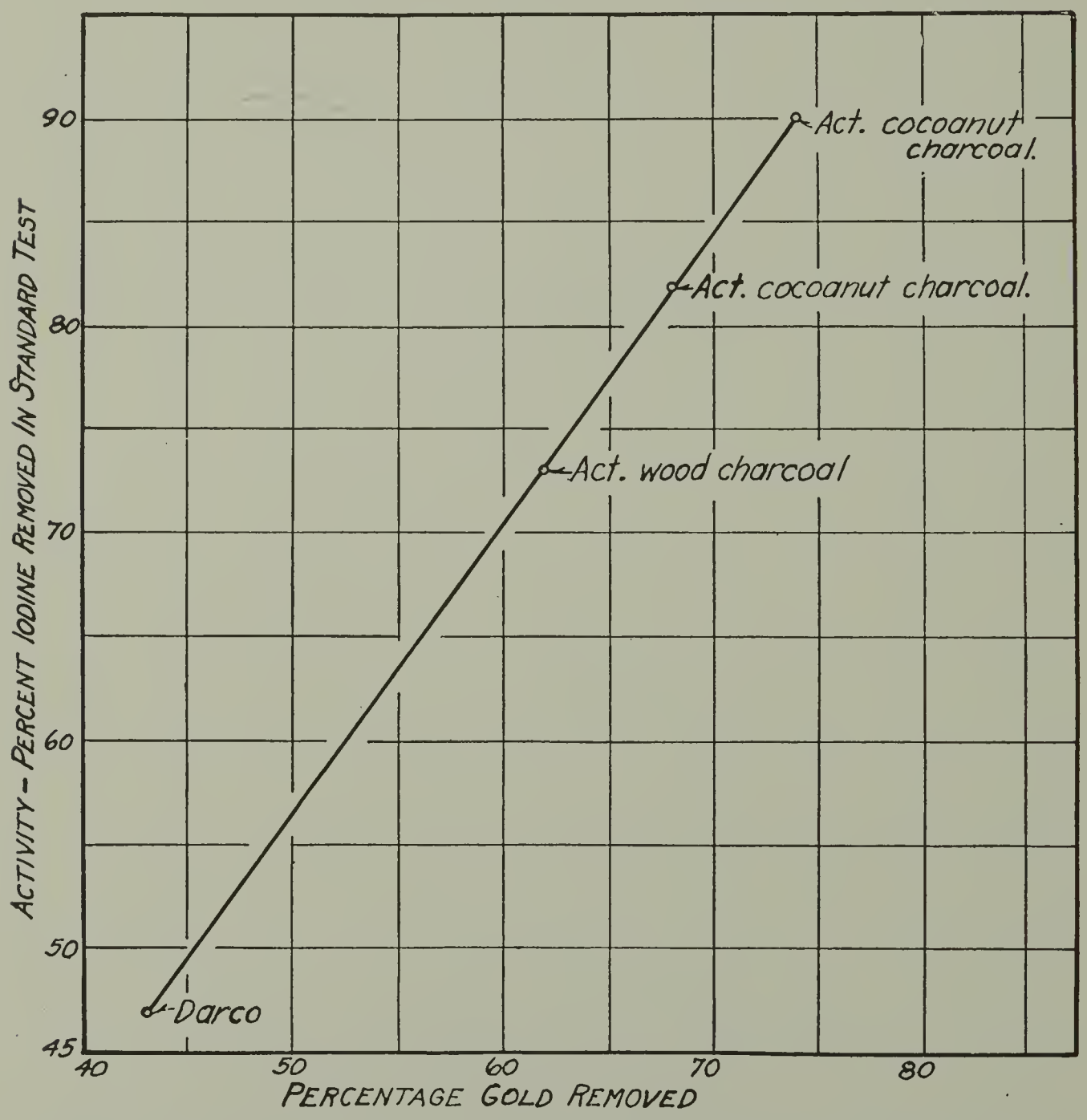


FIG. 6. Removal of gold from gold chloride solution by activated carbon of different activities. All carbons pulverized to pass 200-mesh, acid-extracted, thoroughly washed and dried before testing. Equal weights of carbons agitated with gold chloride solution at 25° C. for 10 minutes.

In discussing the first generalization, we may again refer to Fig. 2, Section II, showing the correspondence between the "retentivity" of active carbon for a specifically adsorbed vapor such as toluol and its capacity for removing iodine from solution. This illustrates the

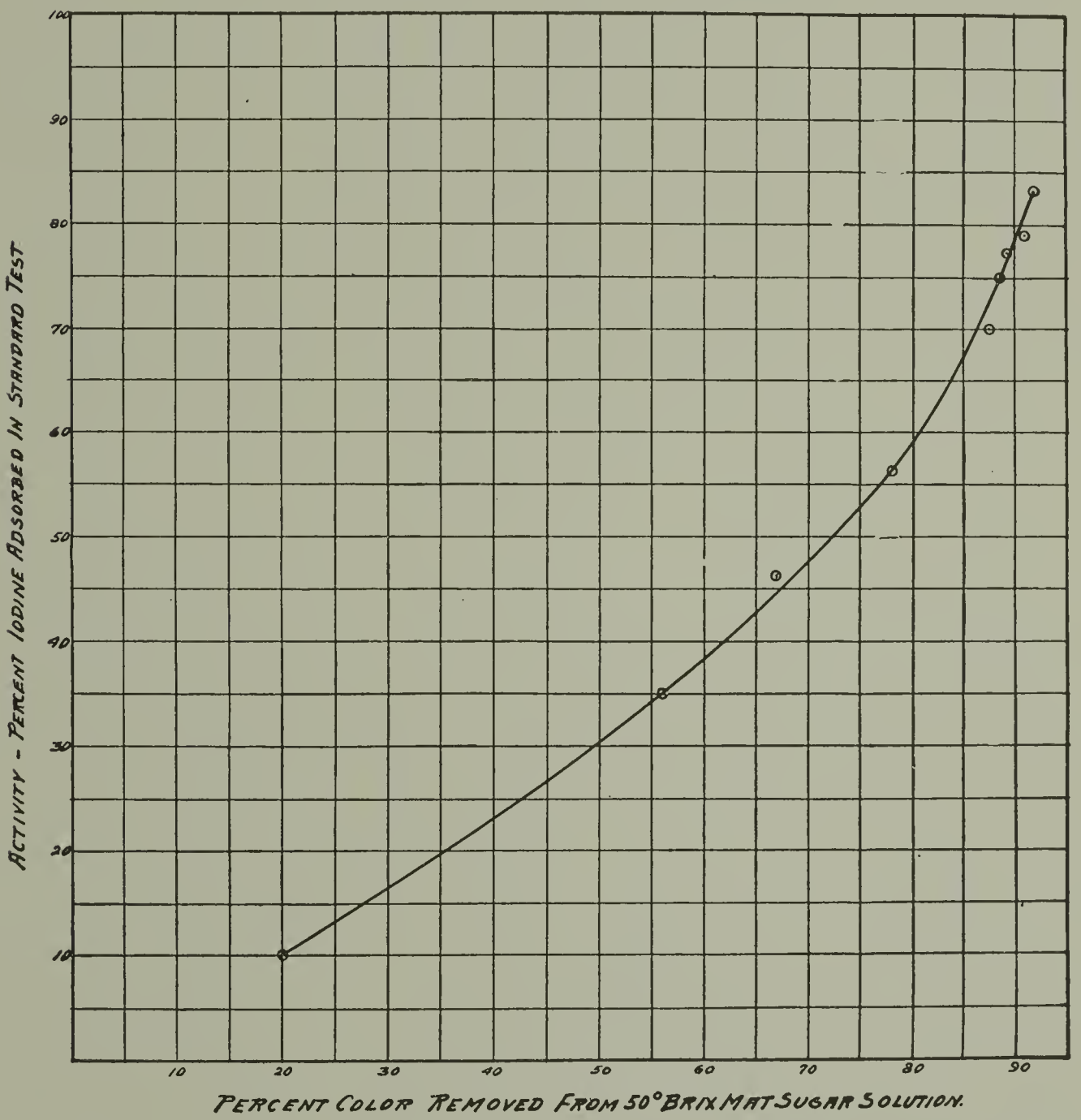


FIG. 7. Relationship between activity and decolorizing power of activated carbons for sugar solution. All carbons of approximately same apparent density, low ash content and pulverized to pass 200-mesh. 5 per cent. carbon on basis of solids present used in decolorizing tests.

parallelism between the specific adsorptive power of carbon for gases and for substances in solutions when the adsorbed molecules are of equivalent dimensions.

Wherever the substances to be adsorbed are of molecular dimensions, we may therefore expect the "retentivity" or the "activity"

as represented by the "iodine number" to be a true index of the performance of any carbon. Fig. 5 showing the removal of a soluble oil from alcohol by carbons of widely varying densities and Fig. 6 showing that the removal of gold from solution is proportional to the retentivity, show how this expectation is realized.

Turning now to the adsorption of particles of colloidal dimensions, we find in accordance with our first generalization that all carbons of equivalent porosity, or apparent density, possess adsorptive capacities for colloidal particles which are directly proportional to their activity, as shown in Fig. 7. If, however, carbons of various apparent densities are considered, no regular correspondence is found between the density or the activity separately and the decolorizing power of the carbon. This is shown in Table 6 where a variety of technical and special carbons are arranged in the order of diminishing decolorizing power for a standard sugar solution, column (4).

TABLE 6

COMPARATIVE DATA REGARDING VARIOUS ACTIVATED CARBONS

All carbons pulverized to pass 200 mesh, acid extracted. Thoroughly washed and dried before testing.

| Nature of Carbon | Apparent Density A.D. (200–270 Mesh) (1) | Activity (2) | Ratio Activity to A.D. (3) | % Color Removed from Sugar Solution (4) | Ash Content (5) |
|---|---|---|---|---|---|
| Act. wood charcoal..... | 0.382 | 73.0 | 191 | 91.0 | 1.44% |
| " cocoanut charcoal.. | 0.548 | 95.0 | 173 | 90.0 | 0.83 |
| " wood charcoal..... | 0.426 | 64.0 | 150 | 89.4 | 2.30 |
| Kelpchar..... | 0.216 | 59.0 | 273 | 88.2 | 12.96 |
| Norite..... | 0.393 | 65.6 | 167 | 88.2 | 3.38 |
| Act. soft coal..... | 0.413 | 60.0 | 145 | 86.9 | 23.75 |
| " wood charcoal..... | 0.472 | 67.5 | 143 | 86.8 | 2.97 |
| " " " ..... | 0.419 | 53.1 | 127 | 86.1 | 0.75 |
| " " " ..... | 0.528 | 65.9 | 125 | 86.1 | 2.15 |
| " " " ..... | 0.376 | 46.5 | 123 | 85.3 | 1.32 |
| " " " ..... | 0.471 | 56.0 | 118 | 85.2 | 0.88 |
| " " " ..... | 0.503 | 58.5 | 116 | 85.4 | 4.03 |
| Darco..... | 0.470 | 44.0 | 93.6 | 85.7 | 36.63 |
| Act. wood charcoal..... | 0.570 | 57.0 | 100 | 83.3 | 1.74 |
| " " " ..... | 0.647 | 62.5 | 96 | 76.5 | 1.04 |
| " cocoanut charcoal. | 0.766 | 72.0 | 93 | 62.3 | 2.14 |
| " synthetic coke..... | 0.714 | 48.5 | 68 | 33.3 | 9.19 |

The order of the densities in column (1) and of the "activities" in column (2) does not diminish with any corresponding regularity. If, however, as in column (3) we take the ratio of the values in

column (2) to those in column (1), we find the values of this ratio lie on a fairly smooth curve when plotted against decolorizing power. This is shown in Fig. 8. In other words, the adsorptive power of

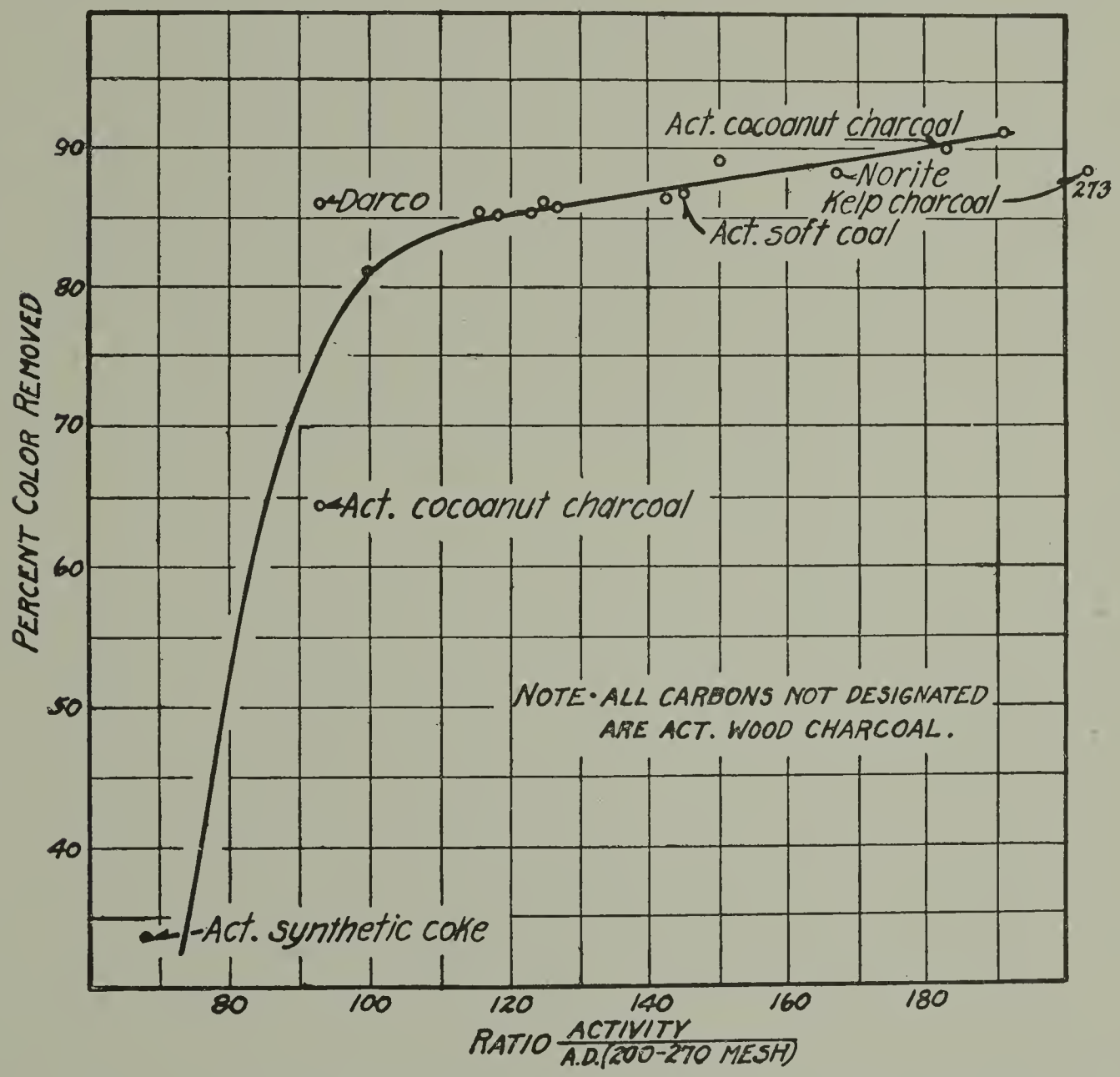


FIG. 8. Relationship between ratio of activity to apparent density and sugar-decolorizing power of activated carbons. All carbons pulverized to pass 200-mesh screen, acid-extracted, thoroughly washed and dried before testing. 10 per cent. carbon on basis of solids present used in decolorizing a very dark 50° Brix mat sugar solution.

carbon for particles of colloidal dimensions is a mathematical function of the ratio of its activity to its apparent density, fineness being constant.

The second generalization, namely, that a given carbon will be most effective as an adsorbent if it carries an electrical charge opposite in sign to that carried by the particle to be adsorbed, will be accepted as axiomatic (27–29). The justification for its statement

is the fact that it accounts for the only variables in the performance of decolorizing carbons which are not adequately covered in the first generalization. Active carbon may either be neutral or may readily become positively or negatively charged by the adsorption of hydrogen or hydroxyl-ions from solution. This explains why the decoloriz-

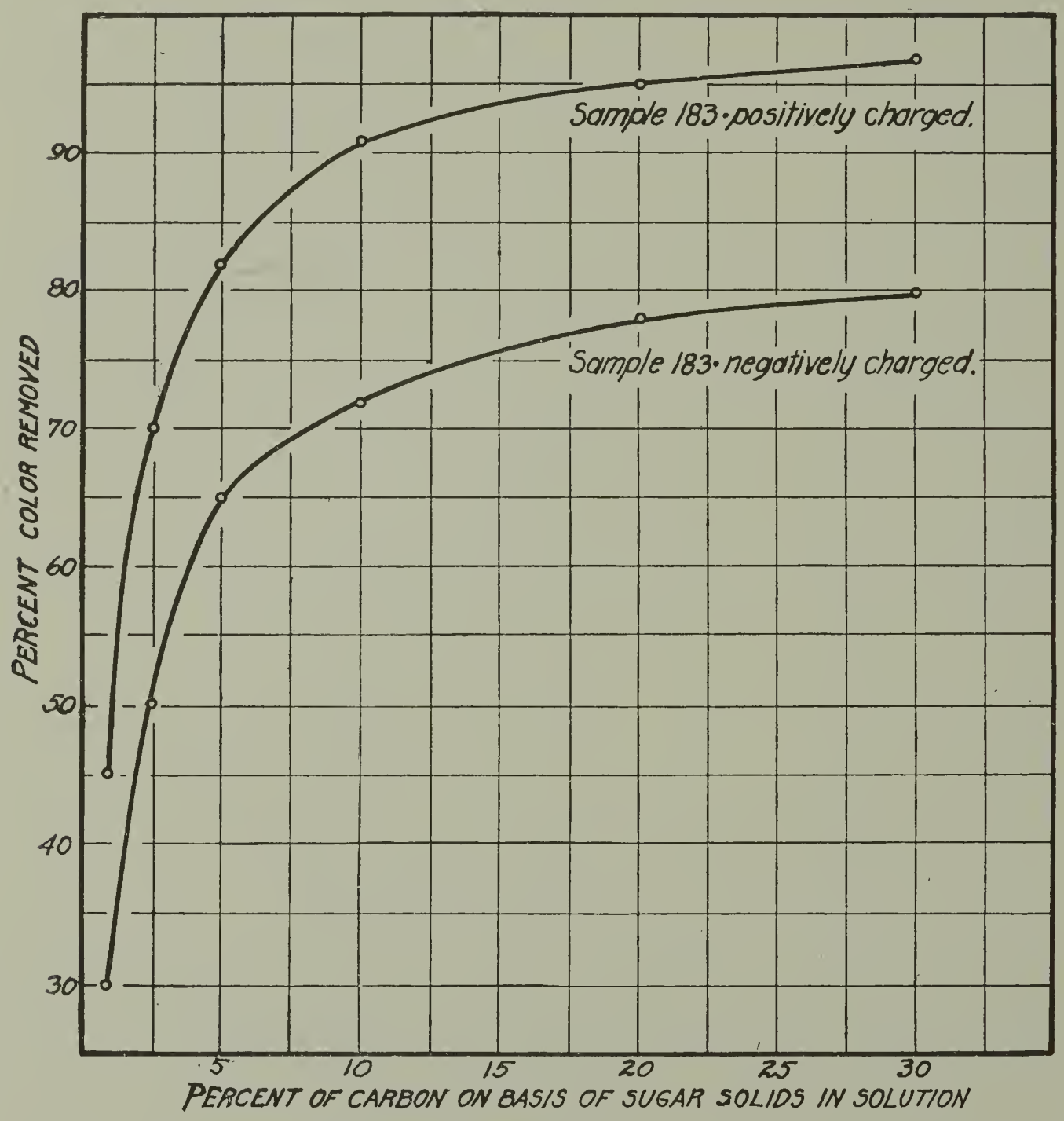


FIG. 9. Effect of electrical charge upon the decolorizing efficiency of activated carbons in 50° Brix mat sugar solution. Carbons pulverized to pass 200-mesh and freed from soluble constituents before testing.

ing power of all carbons for sugar solutions is increased when the solution is acid. The coloring matter consists mainly of negatively charged colloids. On the other hand, the color particles in cotton-seed oil are positively charged, and its acidification decreases the

decolorizing power of the carbon. The carbon may be caused to assume the desired electrical charge prior to its introduction into any given solution or liquid. The effect of such treatment on adsorptive power is shown in Fig. 9 and is also readily demonstrated by the effect upon the adsorption of ionized coloring matters such as Ponceau Red which is positive and Methylene Blue, the colored ion of which is negative.

The somewhat anomalous reverses in the order of decolorizing power observed between different carbons when used for certain oils and in aqueous solution will find complete explanation when the effect of the electrical charge is considered. The fact that a given carbon is electrically charged, for example, does not influence its adsorptive capacity when it happens to be reacting toward neutral particles, but becomes of decided moment when it is employed to adsorb particles which carry an electrical charge.

Since the ability to assume such electrical charges is common to all forms of active carbon, the differences in adsorptive power caused merely by differences in electrical charge on the carbon are not fundamental in estimating the intrinsic character of the carbon. Such effects, nevertheless, have been a fruitful source of confusion in comparative evaluation of many special decolorizing carbons. The generalizations above permit the selection of tests which are criteria of the fundamental properties of the carbon and are not merely peculiar to the special characteristics of a given liquid or adsorbable substance. They also facilitate the intelligent specialization of the properties of the carbon for specific uses by appropriate selection of the raw materials and modifications of the activation processes.

The fallacious character of such generalizations as those attempting to relate decolorizing value to nitrogen content have been adequately treated by others (30). A recent observation (31) attempting to relate the decolorizing power of carbon to the hydrogen content of the carbon is a special case valid only for carbons made by the same process from the same raw material over a limited range of conditions. Its significance depends upon the fact that activation involves the elimination of hydrocarbons by one means or another and therefore increase in "activity" goes hand in hand with a diminished hydrogen content.

*Considerations Affecting the Selection of Decolorizing Carbons*

It will be evident from the preceding section that the physical requirements of a carbon for adsorption from solutions and liquids are much more varied than is the case for gas-adsorbent carbons.

The preferred physical form of the carbon will depend upon such factors as the size of the particles to be adsorbed, the viscosity of the liquid, the nature of the methods required for recovery of the adsorbed material from the carbon and revivification of the latter, and the engineering methods employed for handling the carbon, whether by the tower system, or by filtration or centrifuging the carbon from the liquid.

For removing particles of molecular dimensions from liquids of high mobility, a dense granular gas carbon will be as effective as the finer or more porous forms of equal activation. If the carbon is easily revivified *in situ* by moderate heating, steam, or solvents, the granular type with tower system may be distinctly indicated. As the size of the adsorbed particles approaches colloidal dimensions increasing dispersion of the carbon is necessary. If pulverulent forms of carbon are used, resort must be had to filter press or similar mechanical systems for handling the carbon. Even for the latter type of carbon, however, the physical structure is of vital importance. If the carbon is devoid of structure or too soft and impalpable, it "slimes" the filter, or may go into colloidal solution in certain solvents. Therefore, a definite structure is essential to good filtering properties. Carbons made from raw materials lacking in pronounced structural character, such as soft coal, are generally poor in filtering quality.

Dispersion of solid adsorbents can be accomplished in two ways, one by increasing the porosity of the particle and the other by increasing its fineness. Some forms of decolorizing carbon owe their effectiveness in adsorbing colloidal particles to their extreme fineness, coupled with relatively low porosity and "activity." Others of less minute subdivision owe their value to a higher porosity of particle and higher intrinsic "activity." The latter are superior not only in filtering qualities, but in their more universal applicability, as they are equally effective for particles of colloidal and molecular dimensions.

The viscosity of the liquid is also a determining factor. The rate of adsorption is dependent upon diffusion velocities. It may

be desirable, therefore, to increase the rate of adsorption by raising the temperature, at a sacrifice of total adsorptive capacity. High viscosity in the liquid requires either an increase in the time of contact or in the degree of dispersion of the carbon.

In numerous cases, however, technical success can be achieved only by the use of special types and not all of the commercial forms of decolorizing carbon are in any sense technical equivalents. For example, some decolorizing carbons on the market have no prospective value as sugar decolorizers because of their lack of good filtering properties, although possessing properties which fit them for special uses Where purity, the highest possible activity and high porosity with good mechanical structure are required, steam-activated wood chars are unapproached in quality, but at present are also most expensive. The purification of acids is restricted to those carbons which are both free from soluble ash and of high activity. To prepare organic chemicals of the highest purity, a high activity is usually essential. In many of the heavier and more viscous liquids, such as glycol, a carbon of excessive fineness and softness goes into colloidal solution and cannot be filtered out. In the treatment of edible oils, carbon has an advantage over fuller's earth in that the earthy flavor imparted by the latter is sometimes unpleasing. For water filters at office fountains, etc., a special type of porous block filter can be made. Methods have been developed for preparing bonded blocks of activated carbon of any desired size and porosity. Steel containers of any shape and dimension can be filled with a continuous porous mass of active carbon, eliminating all dusting, packing or settling, such as may occur with loose granular carbon, and possessing extremely desirable mechanical properties for certain uses.

It is further evident that the type of carbon to be selected for a given purpose cannot be considered apart from the development of the appropriate engineering methods for its employment. The high degree to which the mechanical methods of handling bone black have been developed in sugar refining, and the lack of equally well-perfected and successful engineering methods for handling finely powdered materials such as the decolorizing carbons, gives the former its chief competitive advantage. The question of ash removal is not a real factor, because precipitated calcium phosphate is much more effective as an ash remover than is the calcium phosphate in the bone black, just as the best types of activated carbons are

more efficient decolorizers than the carbon in bone black. There is no inherent reason why ash removal and decolorization should be combined in a single operation if the two can be more efficiently performed separately. As the technology of the manufacture of decolorizing carbons of any required type nears solution, the extension of their use has largely become an engineering problem.

To recapitulate, mechanical form and structure have been shown to be as significant as the content of active carbon itself in determining the industrial applications of activated carbon. It has been shown that the required densities of the gas-adsorbent types fall within a relatively narrow range, whereas for employment in liquids the preferred physical properties may vary from the high densities of the ideal gas adsorbent to the high porosity and subdivision desired of a good sugar-decolorizing carbon. The principal reason for this wider range of physical properties required of adsorbents employed in liquids is the enormously wider range in size of particles which the latter type is required to adsorb. The versatility of service expected of this class of carbons can be more clearly visualized by a résumé of a few typical applications.

*Suggested Industrial Applications for Activated Carbon in Liquids*

(1) Making white sugar directly from cane juice; ultimately, its use in part or whole in refineries.
(2) Purification of both organic and inorganic acids, such as lactic, citric, acetic, tartaric, phosphoric, etc.
(3) Purification of a great variety of organic liquids—alcohols, acetone, cane, maltose and glucose syrups, glycerol, glycol, etc.
(4) Decolorization of waxes, gelatine, glue, etc.
(5) Removing objectionable colors and flavors from edible oils and fats.
(6) Decolorizing and purifying petroleum oils.
(7) Water purifying filter, removing tastes, odors and bacteria.
(8) Recovery of rare metals such as gold from dilute solutions.
(9) Recovery of alkaloids from solution.
(10) Pharmaceutical and medical reagents and preparations.

The technical possibility of all of the above uses has been proven on a laboratory scale. Some are in the industrial stage and some depend upon current market conditions, or the requisite engineering development for commercial success.

The pharmaceutical and medical applications are for the most part still in the laboratory stages. A few uses have already appeared. The possibilities of a physically and physiologically inert adsorbent of high purity and high adsorbent activity, non-selective as to water, are so numerous both as a reagent and for direct therapeutical application, that further developments in this field may be reasonably anticipated.

To meet the requirements of this wide range of industrial service, the activation of carbon by the Chaney processes of selective oxidation is uniquely adapted, because it alone possesses the latitude in choice of raw materials and the flexibility of treatment by which any desired combination of physical properties and activation can be secured.

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(See page 353 for discussion)

# ABATEMENT OF INDUSTRIAL STENCHES BY MEANS OF ACTIVATED CARBON

By ARTHUR B. RAY and N. K. CHANEY

Read at the Wilmington, Del., Meeting, June 20, 1923.

There are many industrial processes which unavoidably give off objectionable odors or vapors. Many of us are familiar with the particularly obnoxious odors given off from the processes of rendering slaughter-house waste and other waste fats to recover tallow and have noted from time to time the publicity given to controversies between the health authorities and the operators of these processes. Other industries rather well known by reason of their odoriferous byproducts are the glue, fertilizer, soap, varnish and hide-treating industries. There are also numerous chemical plants which not only give out foul odors but in some cases more or less toxic vapors and gases.

In many cases, plants which give off particularly obnoxious odors and fumes are located in isolated sections as far away from habitation as possible. But obviously such an enforced isolation is rarely economical, so the operators of these plants have tried to satisfy the health authorities by various attempts at abating the nuisance.

Where these processes are operated and attempts are made to abate the nuisance, it is customary to cover or hood the containers and apparatus in which the processes are carried out, and by keeping a positive suction upon them by means of suction blowers to prevent the immediate dissemination of the objectionable odors and vapors. This protects the operators and persons in the immediate vicinity of the apparatus. The question then arises as to what disposal to make of the air laden with obnoxious fumes and vapors.

Various methods of disposing of this foul air have been suggested and tried. One of the simplest schemes is merely to pass the air into the tall stack from the boilers, the idea being that by mixing the foul air with the hot combustion gases from the boilers, some of the foul material will be destroyed and the rest disseminated in such a tenuous form as to cease to be a nuisance. Unfortunately, such a simple scheme does not satisfactorily solve the problem in

the large majority of cases. Very little of the foul matter is destroyed in such a process and although the concentration is reduced, the nuisance is not abated, as many inhabitants of sections adjacent to rendering plants can and do testify vigorously. Putting the foul vapors into a stack really aids in their dissemination over wider areas.

Passing the air laden with foul matter through water sprays has been tried, but, except in certain cases where the objectionable matter such as acid fumes, etc., is readily soluble in water, this procedure is of practically no value. In some cases attempts have been made to mask or neutralize the foul odors given off from certain processes by injecting into the foul air a volatile material having a pleasant odor. Some of the volatile materials used are claimed to disinfect the air as well as mask the foul odors. In other cases, the foul air is passed over pots in which sulphur is burned or tar is boiled and thus is mixed with sulphur dioxide or tar fumes with the idea of reducing the obnoxiousness of the odor.

A recently developed process attempts to render the foul matters innocuous by causing them to react with chlorine. In the successful operation of this process, a careful adjustment of the proportion of chlorine and foul matter must be maintained, since either an insufficiency or an excess of chlorine is undesirable. It is obvious that such a process can be operated only under constant supervision. As a matter of fact, it was developed and intended to be employed in connection with large city garbage and waste disposal plants.

## An Activated Carbon Installation That Proved Satisfactory

It is evident, therefore, that the methods discussed are either ineffective or too complicated for general use. If a rendering plant, for instance, could not by these known means cease to pollute the atmosphere with foul odors when ordered by the health authorities to do so, it had no alternative but to shut down. This was the situation exactly when we were asked by the officials of a rendering plant to devise some means that would permit the plant to operate without disseminating the foul odors which had prompted the order to abate the nuisance or shut down.

It was an emergency, and we acted accordingly by hastily designing, with very little data to guide us, an installation which was rather crude from an engineering standpoint but which we thought

would solve the problem. It did. The fumes and odors from the rendering kettles are caused to pass into a bed of activated carbon which absorbs them completely. When the carbon, after use for some time, becomes saturated with the impurities it is revivified *in situ* and used for another period.

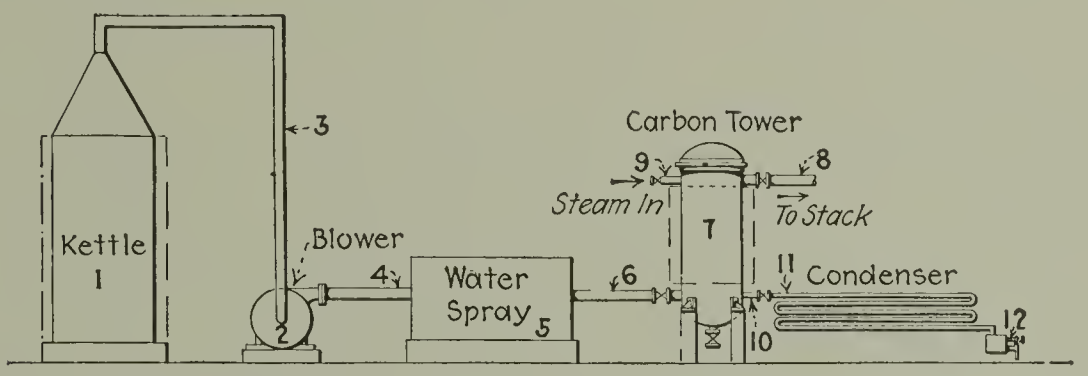



FIG. 1. DIAGRAMMATIC LAYOUT OF STENCH-ABATING INSTALLATION USING ACTIVATED CARBON

After the erection of the installation in October, 1922, the plant officials and the town authorities expressed their perfect satisfaction with its operation.

## TYPE OF ACTIVATED CARBON EMPLOYED

The activated carbon successfully used in the installation is a granular, highly activated coconut charcoal of around 8 to 14 mesh. This carbon is the best for the purpose because (1) it has a high absorptive capacity for odors and vapors; (2) it selectively absorbs the organic and odoriferous substances in preference to water vapor; (3) it is mechanically strong and so resists crushing and abrading action; and (4) it is relatively dense so that a minimum volume has a maximum absorptive efficiency.

## OPERATION OF INSTALLATION

An elevation of the installation is shown in Fig. 1. Reference numeral 1 denotes a closed rendering kettle which is the source of the objectionable odors or fumes. Blower 2 draws the kettle fumes through pipe 3 and forces them through pipe 4 into chamber 5, where they are cooled by passage through a water spray. A draw-off pipe is provided at the bottom of this chamber and leads to a sewer. The cooled gases and fumes with or without drying then pass through pipe 6 to the purifying tower 7, which contains granular activated carbon. The gases from which all obnoxious matter has

been removed by the activated carbon are then discharged in the air through pipe 8.

When it becomes necessary to revivify the carbon, it may be heated by any suitable means, but preferably by passing steam through it, to cause it to release the impurities it has taken up. In the installation shown, steam under 15 to 25 lb. pressure enters through pipe 9, passes downward through the carbon and out through pipe 10. The discharged steam is run to condenser 11 and the condensate trapped off into a sewer. Any uncondensed steam or other vapors and fixed gases are passed through pipe 12 into the firebox of the boiler used in generating steam for the plant or are otherwise readily burned under conditions to insure complete combustion. The revivified carbon is cooled by passing cold air or water through it and is then ready for re-use. If desired, the carbon may be dried by passing air through it while it is hot.

The details of construction of the carbon tower employed in the emergency installation are as follows: The cylindrical container of $\frac{1}{4}$-in. steel is provided with a horizontal partition in grid form in its lower portion. On the grid are placed a 4-mesh galvanized iron wire screen and a 20-mesh brass wire cloth to support the carbon. Similar screens are placed on top of the carbon to prevent particles of carbon from being carried upward by the ascending gas current. The top screens are weighted and freely movable so that they may follow the charge if it settles. Valves control the inlet and outlet of gases and are closed during the revivifying operation. Other valves control the inlet and outlet steam or hot water used in revivifying the carbon and are closed during the absorbing operation. A draw-off pipe with valve is also provided in the base of the tower. A 6-in. flanged pipe is provided for withdrawing the carbon at any time. The tower is jacketed with heat-insulating material to reduce radiation losses during revivifying operation. The tower as it appeared installed is shown in Fig. 2.

## General Principles Applying to Any Installation

It is obvious that the dimensions and details of construction of the carbon container and the general arrangement of the apparatus may be varied to meet the needs of a particular installation. The amount of carbon used and the depth of layer may be varied. A number of small towers may be used in series or parallel. The foul air may be sucked through instead of blown through. The foul

gases may be cooled by passing through coils externally cooled by air or water. If cooled by passage through a water scrubber, the gases may be dried by passage through a drying agent such as lime or calcium chloride. It is pointed out, however, that drying is not necessary, since the carbon selectively absorbs organic vapors and particles in preference to water vapor and will, therefore, effectively purify foul air which carries a large amount of water vapor.

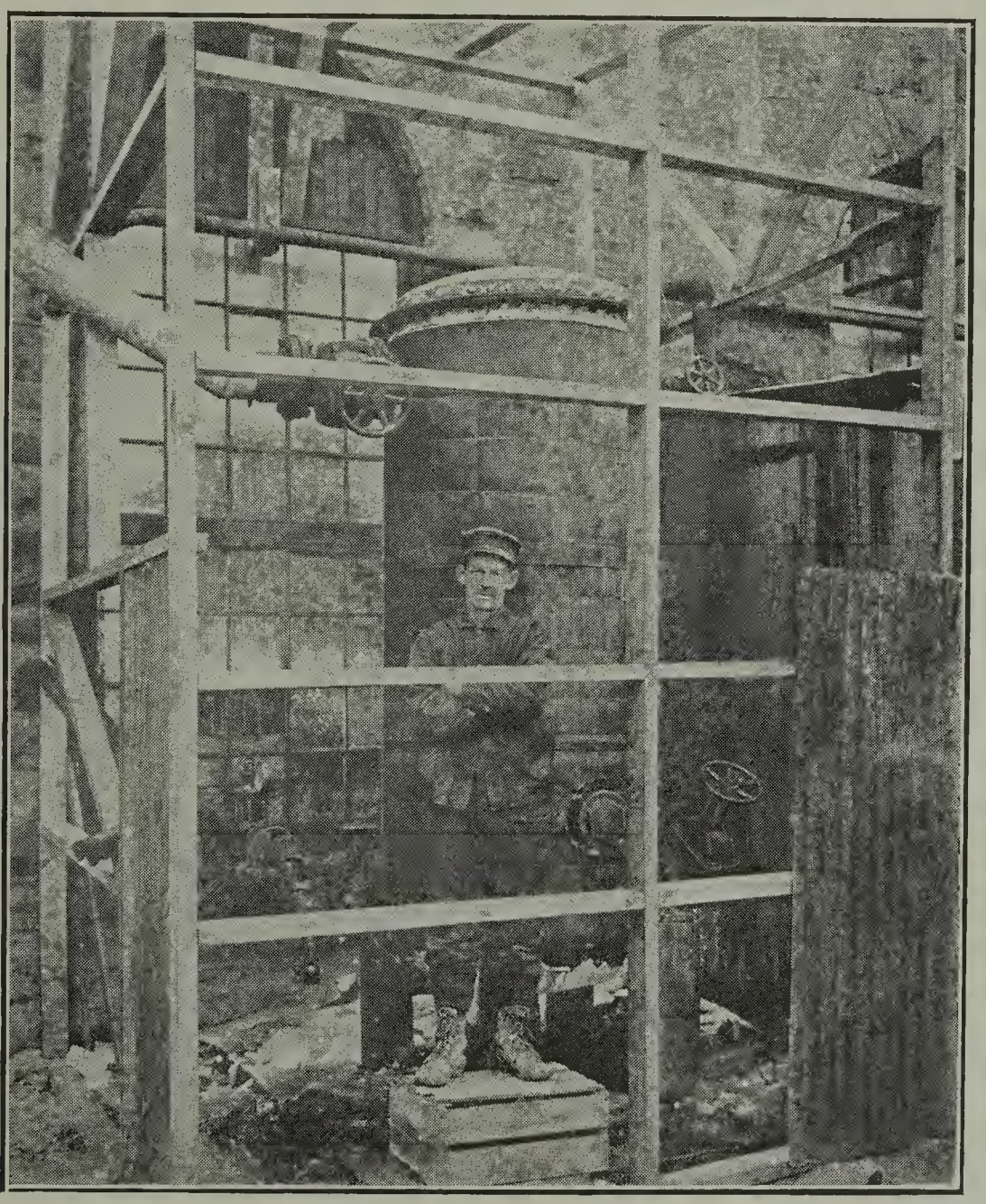


FIG. 2. ACTIVATED CARBON ABSORBER (CONTAINS 1,000 LB. OF GRADE 4 CARBON, 8–14 MESH)

The particular installation described was not designed for continuous operation, because the plant is not operated continuously. There is ample time at this plant for revivifying the carbon and getting it ready for re-use between the operating periods. However,

if continuous operation is desired, the carbon tower may be duplicated and suitable connections and valves added so that one tower may be in operation while the carbon in the other is being revivified.

The length of time which the carbon may be in service before it becomes saturated with the foul substances and must be revivified will, of course, depend upon the amount of foul materials passed in per hour. The capacity of the carbon for absorbing and retaining the foul materials is very large. It will take up and retain more than 50 per cent of its weight of certain vapors. So, since the actual weight of foul materials in the air is usually very small, the carbon will remain effective for a considerable time. At the installation described, it has been the practice to revivify the carbon once a week, but the indications are that the carbon is not saturated by a week's use, and that the periods between revivifications could be longer.

## No Attention Necessary

The installation requires no attention during operation. The only power required is that necessary for the operation of the suction blower which keeps a suction on the kettles, etc., and which forces the foul air through the bed of carbon. The resistance of the carbon to the passage of air is of course dependent upon the depth of bed and volume of air passed per sq. ft. per minute. It has been determined by actual plant operation that the pressure drop through a bed of 8 to 14-mesh carbon 5 ft. deep is approximately as follows:

2.25 lb. when 75 cu. ft. per sq. ft. is passed
1.25 lb. when 50 cu. ft. per sq. ft. is passed
0.5 lb. when 25 cu. ft. per sq. ft. is passed

The passage of 150 cu. ft. of air per minute through a cylindrical bed of 8 to 14-mesh carbon 5 ft. deep and 3 ft. in diameter will require a pressure of around 0.5 lb. This rate is sufficient to keep a positive suction on several vats or kettles, for instance, and can be obtained by the use of a small Roots positive blower or other suitable blower.

The total cost of operation includes the cost of operating the pressure blower, supplying, if necessary, cooling water to cool the air and vapors before they enter the purifier, heating the carbon in the revivifying process by introducing steam or hot water or by other means, and cooling the carbon by passing cold air or water

through it. Without going into details, it is obvious that the total operating cost is very small.

## Conclusions

We have demonstrated that industrial stenches can be effectively abated by the use of a simple installation employing activated carbon as the absorbing medium. Highly activated granular coconut charcoal is the type of carbon successfully used. The original cost of the installation is not large and the operating cost is very small. The installation requires no attention except during the periodical revivification, which is carried out by simply heating the carbon *in situ* by steam or other means. The signal success of the installation now in operation leads us to believe that the principles employed in this case may be applied to solving similar problems at other plants and may be of real value to those industries which are so unfortunate as to have obnoxious fumes and odors for disposal. With such an installation available, there is no reason why any industrial process should be operated so as to pollute the atmosphere with foul odors.

The authors desire to express their appreciation of the engineering assistance given by Mr. H. D. Edwards, of the Linde Air Products Co.

Union Carbide and Carbon Research Laboratories, Inc.,
Long Island City, N. Y.

## Discussion

President Howard: This concludes the group of papers on activated carbon. The group is now open for discussion.

Dr. Ralph H. McKee: Mr. President and members of the Institute and guests: I wish to bring out some facts which I believe do not agree with the theories which have been presented, regarding "activated carbon." The first fact, I may add, is somewhat from hearsay evidence as I have not carried out, myself, the experiments I shall refer to. The speakers have stated that on heating at high temperatures to drive off hydrocarbons it is necessary to have access of air or steam if one is to get "activated carbon." The experiments I have in mind are those where oil shale is heated to get oil, where a much lower temperature is used than has been suggested. The American Shale Reduction Co., in their small plant, use only a temperature of approximately 450°C., which is far lower than agrees

with the theories just presented. Also, they are heating it out of contact with any air or steam, except that contained in the shale. In other words, it seems to me that the explanation of the activation of the carbon by the partial oxidation of the hydrocarbons and residual carbon is not correct, because the shale residue which has been heated only in a reducing atmosphere and which contains some twenty per cent of carbon is a quite active material, so far as concerns properties which are ordinarily stated to be those of activated carbon. It is used for decolorizing oil and can be used in purifying other liquids. It does not seem to me that the activation of this carbon agrees with the theories suggested here.

Again, passing now to something with which I have personal knowledge, we find we can change carbons from one type of activity to another with very mild treatment, too mild treatment to change the capillary conditions of the carbon. For example: if we take a carbon such as almost any of those of the acid-treated carbons mentioned, such as superfiltchar, these products absorb the coloring materials present in sugar and similar solutions. Now, if we take that carbon, or even ground wood charcoal, and heat it to a red heat with a small percentage of sodium carbonate and then wash out the sodium carbonate, we have a carbon which has quite different properties. This new carbon will no longer readily remove the color from sugar solutions but it is a carbon which will remove gold from a cyanide solution many times more rapidly than the original carbon did, perhaps sixty or eighty times more rapidly.

If we take this same carbon which has been treated with sodium carbonate and boil it in 0.25 per cent acid, the carbon that we will then have will no longer readily pick up gold from a cyanide solution, but it now has had returned to it its original activity and will now remove the coloring materials from a sugar or other solution.

No one would pretend that heating at a temperature of 100° C. with 0.25 per cent acid would change the capillarity—or change the carbon. And yet we have here a carbon which is commonly called inactive, though it will pick up a positive ion in a special experiment, and in the other case we have a carbon commonly called "active" and which will pick up a negative ion. If the explanation proposed was one possibly of electric charge it might be quite different. I may add that I have not a theory to propose. I am simply bringing out some facts which I believe do not fit into the theory given of "graphitic" and "pseudographitic" carbon, or other of the theories

suggested; because I can not think that these two carbons, graphitic and pseudographitic, are anything but slightly changed carbons whose differences are only incidently concerned with the activity of the carbons.

Let us go a little further. These carbons when they absorb gold from a cyanide solution, or silver from a silver cyanide solution, or copper from its cyanide solution, absorb roughly in proportion to the atomic weights of gold, silver, and copper. It makes one think of Loeb's ideas on gelatine. It is hard to think of carbon forming tautomers, yet that is what we would say if it was in the field of ordinary organic chemistry.

If we use on a vitamine solution the alkali-treated carbon which adsorbs gold, we will take up one portion of the vitamine B, the anti-neuritic portion. But this carbon does not adsorb the growth-controlling portion of the vitamine B. If on the other hand we take the same carbon and treat it with a small amount of acid, and then rewash it with water, it will no longer pick up the portion of the vitamine which it formerly picked up, but it picks up now the growth-controlling portion and lets the anti-neuritic go through. These are interesting facts, details of which will be published later. It seems to me that these facts do not agree with the graphitic and pseudographitic suggestions which have been made as to the theory of carbon activation.

Let us go further. In the case of carbons, as has been stated here, the general belief has been stated that gas activity and gas absorption are rather closely related to the other properties of the active carbon, for example, the removal of color from solutions and oils and so forth. I wish to call attention to the fact that the chemical activity of the carbon in the sense of catalytic activity is not at all closely related. For example, the cocoanut charcoal and the gas mask charcoal are charcoals which have been indicated as quite highly activated carbons. Some of the others, like the acid-treated wood charcoals, are indicated as less activated, but when one comes to use them for catalytic purposes the very reverse is true. Products of the types spoken of as most highly active, the highly "activated" carbon, such as cocoanut charcoals, bachite, one now much used by the Chemical Warfare Service, whetlerite, and others accounted as most active, are only one-fortieth as active catalytically as some of those of very weak activity as measured by gas absorption.

In other words, it seems to me that many of those who have worked in this field have been inclined to place far too much emphasis on gas absorption and to look at the question of the activated carbon field almost alone from the side of gas absorption. There are several other fields in which activated carbons are important and a proper theory of "activation" must take the facts in all fields into consideration.

DR. FREDERICK BONNET, JR.: I think Dr. McKee brought out some interesting points in regard to oil shale. I think, however, that one point has been missed. Why ascribe the decolorizing action solely to the carbon left behind in the shale instead of to the shale itself? Many other substances besides carbon have considerable adsorptive capacity, for example, fuller's earth, and I think Dr. McKee's decolorizing power may be due largely to the ash which is left behind in the shale. Adsorption is well shown by shaking a clean glass bottle or flask with a solution of methyl violet. After the solution is poured out of the flask and the flask is washed thoroughly with water, a thin violet film remains on the surface which cannot be washed out with water. It is adsorbed on the surface. After a very small quantity of alcohol is added, the methyl violet leaves the glass surface, due to a change in the interfacial surface tension. The same phenomenon is indicated in the purification of alkaloids by decolorizing carbons and in the separation of vitamins A and B. Some of the other points brought out by Dr. McKee Dr. Chaney will doubtless answer.

DR. W. A. PATRICK: We must remember that adsorption from solution with charcoal as the adsorbent does not take place according to a single mechanism. There is the possibility of polar adsorption, i.e., ion exchange, between the ions of the solute and the ions of the ash or of the salts of the organic acids in the charcoal. This polar adsorption would easily explain the experimental results mentioned by Dr. McKee, there being an exchange of the sodium ion for the ions of the heavy metals of the solute.

Silica gel may be made to function in the above manner by soaking in dilute alkali. The well-known permutite metathesis is an extreme example of the same phenomenon.

Another method by means of which the adsorption of salts of heavy metals is brought about by charcoal is the reduction of these salts by reducing gases held in the charcoal. (Professor Hulett has shown the impossibility of obtaining gas-free charcoal.) Silica gel

in its ordinary state will not "adsorb" silver from $AgNO_3$ solutions; however, if the gel is treated with hydrogen at low temperatures, it acquires the property of reducing, i.e., "adsorbing," silver from $AgNO_3$ solutions.

From the above it can readily be understood how complicated is the nature of adsorption from solution with charcoal, especially when it is recalled that in addition to the above effects we have the complicated question of the wetting of the more or less oily surfaces, producing a change of solubility of the solute by means of capillarity.

MR. H. O. CHUTE: I desire to call attention to an industry of producing and using activated carbon which was in use long before the war. All the books said and many knew that American whiskey was purified by the use of charcoal but no book said nor did many people know that this charcoal was necessarily activated.

The hardwood charcoal, as made in retorts, was reburned in a stone or brick kiln till about twenty per cent of its weight was lost. The heat developed was very great but could be controlled by blocking up more or fewer of the holes in the brickwork at the base of the kiln. Water could also be poured around the base of the kiln, and whatever amount of steam was needed was furnished by the evaporation of this water. It is evident that all the factors of heating, treatment with steam or air or other gas, and cooling by blocking up the air holes and cooling away from the air which was performed in nichrome retorts during the war could be done with these cheap kilns but at the expense of 25 per cent of the coal used. As the coal used was worth only about ten dollars per ton its loss was inconsequential.

Whether the consuming of part of the coal by air was necessary to produce activation I do not know, but it was necessary to the process. This activated charcoal was ground rather fine and put in cast iron vessels and the whiskey was pumped through under high pressure. Purification may have been due to absorption of the occluded gases or oxidation of aldehydes, but was not due, as usually stated, to removal of fusel oil, for this remained in the whiskey and was removed by subsequent distillation and sold.

PRESIDENT HOWARD: I should like to ask Dr. Ray how long that column in his direct treating device would work without being revivified, and whether the material is just as good after repeated revivification? And, if the gas which is taken off during revivifica-

tion is burned under the boiler, why the original fumes could not have been burned under the boiler?

DR. RAY: Replying to President Howard's first question regarding the stench-abating installation, I will say that the carbon used in the installation described is revivified at least once a week. Speaking generally of activated carbon stench-abating installations, the length of time between revivifications will depend upon the ratio of carbon to amount of odoriferous material brought in contact with it. Since, as a rule, the actual weight of this material given off per day is relatively small, the carbon may be used for a relatively long period of time before it becomes saturated.

Recent tests of the carbon which has been in service for over eight months and which has of course been revivified many times showed it to be as good as when put in service.

Replying to the second question, the reason why the odors as originally sucked out by the ventilating system cannot be economically destroyed by burning is that they are mixed with a very large volume of air. The objectionable gases and vapors which are released from the carbon when it is revivified are concentrated and can be readily destroyed by passing them into the firebox of the boiler.

DR. CHANEY: I think when Dr. McKee has an opportunity to go more carefully into the details of our paper he will find many of the questions which he has raised completely answered.

The question of decolorizing value of oil shales after low temperature carbonization is complicated, as Dr. Bonnet points out, by the fact that the product is a mixture of mineral ash and carbon in which the properties of the carbon would have to be determined when isolated from the preponderating mineral content before their bearing upon the present discussion could be determined.

We have referred in the paper to activation by calcination at high temperatures and to activation by calcination at lower temperatures in the presence of active mineral salts. The conditions for such activation are most favorable when a small percentage of carbon is dispersed over a large excess of mineral matter as in bone char, for example, where the latter may exert catalytic effects upon the decomposition reactions and almost anything may happen without contradiction to our fundamental postulates.

The importance of the electrical charge upon the carbon in determining the adsorptive behavior of carbon with respect to charged colloids conditions is fully discussed in the paper. We do

not, as Dr. McKee seems to suggest, assume a difference in carbon constitution for each variant in adsorptive behavior. All varieties of adsorptive carbon belong in one class—the pseudo-graphite class—as regards ultimate constitution and all inherently non-adsorbtive varieties of carbon, except diamond, belong to the graphitic class. The object of our paper is to show how many long standing anomalies and contradictions in the behavior of adsorbtive and decolorizing carbons can be rationalized and coherently related. Dr. McKee prefers to return to the original chaos of unrelated observations from which he admits no hope of emerging.

Finally, with respect to the alleged failure of our theories and data to explain the anomalies of catalytic behavior we plead guilty. When it is proved that catalysis is a simple function of adsorbtive power or activity we may properly be asked to show why our data do not completely solve the mysteries of catalytic action so far as carbon is concerned.

If there be phases of catalytic phenomena depending solely upon adsorptive activity we shall expect our data to prove helpful. It is difficult to see, however, what bearing our lack of evidence in regard to catalytic phenomena has to do with our conclusions as to the nature of adsorptive activity in carbon.

DR. RAY: As Dr. McKee has pointed out, the difference in adsorptive characteristics of activated carbon caused by a simple treatment with alkali or acid are certainly not due to any actual change in the carbon itself. As brought out in our paper, the available evidence indicates that the adsorptive power of all activated carbons is fundamentally dependent upon their content of accessible active carbon, which is believed to be a definite modification of carbon. But we also showed that ions and colloidal particles carrying electrical charges are most effectively adsorbed by active carbon which carries an opposite electrical charge. Treating the carbon with acid or alkali is one way of causing the carbon to assume a positive or negative charge in liquids. So the facts, as pointed out by Dr. McKee, that alkali-treated carbon has a special selective adsorptive power for a positively-charged ion such as gold and that an acid-treated carbon is especially effective for adsorbing the negatively-charged colloidal coloring matters from a sugar solution are in perfect agreement with our theories of adsorption by activated carbon. The fact that acid- and alkali-treated carbons assume different electrical charges also quite probably explains why carbons

so treated may adsorb the different vitamine constituents mentioned by Dr. McKee. The two constituents quite probably carry different electrical charges. The carbon which Dr. McKee found would adsorb both constituents was probably approximately neutral.

The illustration of the effect of varying the electrical charge of a carbon given in our paper (Fig. 9) may be referred to here. It is obvious that when a carbon is so treated as to cause it to assume a position charge in a sugar solution its ability to remove color is much greater than when it is caused to assume a negative charge.

DR. MCKEE: How did you make your change?

DR. RAY: By acid and alkali treatment.

DR. MCKEE: On the carbon and not on the sugar?

DR. RAY: The carbon was treated and then thoroughly washed.

Although the ability of activated carbon to remove gold from solution may be affected by the kind of electrical charge which it assumes in the solution, it is interesting to note that carbons having the same charge will remove the gold in proportion to their activity. This was shown in our paper (Fig. 6). The several carbons tested varied greatly as to porosity and origin but they were all treated so as to cause them to assume a similar electrical charge in the solution. Under these conditions the adsorptive power is certainly a function only of the activity.

DR. MCKEE: I found that any carbon would remove gold chloride but that the differential and amount were different.

DR. RAY: It is a fact that gold is more easily removed from the chloride than the cyanide solution but I found that the amount removed by carbons from either solution is a function of the activity of the carbons carrying similar electrical charges. Ordinary wood charcoal has a slight activity so it does remove some gold.

PRESIDENT HOWARD: We will call this discussion closed and proceed to the next paper.

# SOME NOTES ON THE ACTION OF FULLER'S EARTH ON VEGETABLE OILS

By DAVID WESSON

Read at Wilmington, Del., Meeting, June 22, 1923.

The literature shows various reasons and theories for the action of fuller's earth in removing the coloring matter from oils, but unfortunately we are too short on one sort of facts and too long on another to make the theories fit them properly. The object of this paper is to call attention to some unpubiished observations which may assist others eventually to solve the problem.

In factory control it is quite important to know how much oil is left in the spent earth after it leaves the filters. If the sample be first extracted with gasoline or petroleum ether only the the absorbed oil will be removed. If the gasoline extracted earth be next treated with alcohol, a reddish, gummy, sticky material resembling oxidized oil is removed. Acetone is a better solvent than alcohol and is commonly employed. Probably toluene or xylene would be as good, or better, solvents.

If the earth has been used on an oil containing much soap the alcohol extract will consist largely of soap with more or less of the red oxidized oil. For a long time this acetone extract was considered the coloring matter of the oil.

About three years ago, when trying some intensive bleaches on cottonseed oil, it was noticed that when very large quantities of earth were used in proportion to the oil, the apparent amount of coloring matter removed as shown by the analysis of the spent earth was in proportion to the amount of earth used, while the color of the oil was only slightly altered, if at all.

Starting with a bleached oil having a Lovibond color of 25 yellow, 2.5 red, the following results were obtained:

A second experiment made on Wesson Oil gave similar results, shown in Table II.

TABLE I

PER CENT ACETONE EXTRACT

| Per Cent of Earth (Based on Wt. of Oil) | On the Earth | On the Oil | Color | |
|---|---|---|---|---|
| | | | Y | R |
| 5 | 3.64 | 0.182 | 23 | 2.3 |
| 15 | 2.90 | 0.436 | 22 | 2.2 |
| 50 | 1.50 | 0.752 | 25 | 2.5 |
| | | Color of original oil | 25 | 2.5 |

The spent earths were washed with benzene instead of gasoline which accounts for the low acetone extracts.

TABLE II

PER CENT ACETONE EXTRACT

| Per Cent of Earth (Based on Wt. of Oil) | On the Earth | On the Oil |
|---|---|---|
| 5 | 3.65 | 0.182 |
| 15 | 2.92 | 0.437 |
| 50 | 1.00 | 0.751 |

These remarkable results indicated that the earth must do something besides remove color, and must produce an oxidized or polymerized material from the oil itself and remove it by adsorption.

Some experiments made about a year later to determine the nature of the extractable matter in spent earth showed it could be divided roughly in three portions. The analytical results are given in Table III.

TABLE III

| Gasoline Soluble Acetone Extract | Acetic Acid Absorbed, % | Equivalent % Iodine | Iodine No. | Sum |
|---|---|---|---|---|
| | 3.95 | 8.31 | 90.45 | 98.80 |
| Gasoline Insoluble Acetone Extract | 6.36 | 13.45 | 79.30 | 92.80 |
| Gasoline Soluble Benzene Extract | 4.34 | 9.18 | 86.5 | 95.80 |

These figures indicate that the material held by the earth consists largely of oxidized fats. If the earth has an oxidizing or polymerizing effect on the oil it would seem that some light might be thrown on the subject by repeatedly bleaching the same oil with fresh earth and observing the amount of extractable matter in the earth after each bleach, and also recording the color of the oil after

each successive bleach. It was considered desirable to note the variation in this respect due to different earths.

Seven earth samples were obtained representing wide variations in locality and preparation. Samples 6 and 7 were received too late to have as much work done with them as on the first five. The oil used in the experiments was a bleached cottonseed oil taken from the filters in the commercial refining process. It had been bleached with standard *XL*/000 English Earth. The procedure was to bleach the oil three times successively with fresh portions of each earth and determine the amont of acetone extract of the gasoline washed earth after each bleaching.

The results briefly stated were

1st: With the exception of one earth there was no improvement in color after the first bleach. In the case of a very fine Florida earth there was a great darkening in color with each successive bleach.

2d: The adsorption on the various earths averaged 8 to 10 per cent of the earth on each bleaching. The adsorption on the Filtrol and Death Valley Earth was 16.63 and 31.38 percent respectively. The loss by adsorption calculated on the oils ran 1.15 to 1.73 per cent except in the two cases mentioned where it ran up to 2.49 per cent and 4.71.

It seemed reasonable to suppose, if the oxidation theory of bleaching were correct, that adsorbed oxygen on the surface of the earth particles would account for the adsorption. To test this out, five gram portions of the different earths were shaken up with warm water and a weak solution of ammonium ferrous sulphate was run in from a burette until a drop taken out gave a blue color with sodium ferro-cyanide. The results showed that the best bleaching earth, which gave the highest adsorption, showed the lowest oxidation effect on the ferrous sulphate. The oils after final bleaching were titrated for acidity. The best bleaches showed the highest free acid. The summarized analytical and other data are given in tables 4 to 10.

The conflicting results show that there is still much work to be done before we understand fuller's earth.

Grateful acknowledgements are due Mr. Geo. A. Pierce who carried out many of the experiments and performed much of the analytical work.

## TABLE IV

The fuller's earths investigated were well-known standard earths as follows:—

1. XL/000, the standard English earth from L. A. Salamon and Bro.
2. Georgia fuller's earth from Lumpkin, Ga., a 100-mesh American earth.
3. Floridin Earth No 975 from Pomeroy and Fisher, a standard American earth used largely for petroleum as well as vegetable oils. This earth was very finely ground (200 to 400 mesh).
4. Floridin Earth XXF from Pomeroy and Fisher—a coarser grade than No. 975. The regular product.
5. Pikes Peak Earth from Dry Branch, Ga.
6. Filtrol, a new bleaching earth made artificially in California.
7. Another artificial earth from California. A Death Valley clay furnished through the courtesy of Mr. R. T. Goodwin, Elizabeth, N. J.

## TABLE V

COLOR OF SUCCESSIVE BLEACHES AS SHOWN BY EASTMAN COLORIMETER

| | | A (red) | B (yellow) | C (neutral) | Free Fatty Acid as Oleic |
|---|---|---|---|---|---|
| Original Oil..... | Beginning | 2.0 | 50.0 | 0.0 | 0.10 |
| | End | 5.0 | 50.0 | 0.0 | |
| XL/000..... | Bleach No. 1 | None | 33.6 | None | |
| | Bleach No. 2 | None | 34.4 | None | 0.02 |
| | Bleach No. 3 | None | 35.0 | None | |
| Georgia Fuller's Earth | Bleach No. 1 | None | 39.8 | None | |
| | Bleach No. 2 | None | 41.0 | None | 0.16 |
| | Bleach No. 3 | None | 50.0 | None | |
| Floridin Earth, 975—200 mesh..... | Bleach No. 1 | 19.0 | 50.0 | 12.4 | |
| | Bleach No. 2 | 31.6 | 50.0 | 20.8 | 0.02 |
| | Bleach No. 3 | 42.6 | 50.0 | 26.0 | |
| Floridin Earth, XXF—Regular..... | Bleach No. 1 | None | 36.0 | None | |
| | Bleach No. 2 | None | 37.8 | None | 0.004 |
| | Bleach No. 3 | None | 45.0 | None | |
| Pikes Peak (Georgia) | Bleach No. 1 | None | 33.6 | None | |
| | Bleach No. 2 | None | 35.0 | None | 0.15 |
| | Bleach No. 3 | None | 40.0 | None | |
| Filtrol..... | Bleach No. 1 | None | 30.0 | None | 0.25 |
| Death Valley Earth.. | Bleach No. 1 | None | 22.0 | None | 0.22 |

## TABLE VI

### Examination of the Original Earths

| Earth | XL 000 | Georgia Earth | Floridin 975 200 mesh | Floridin XXF Regular | Pikes Peak | Filtrol Earth | Death Valley |
|---|---|---|---|---|---|---|---|
| Loss of weight 105–110° C% | 10.26 | 4.85 | 6.87 | 6.62 | 6.39 | 8.02 | 6.97 |
| Loss of weight on ignition % | 8.10 | 3.60 | 10.71 | 9.20 | 5.09 | 5.81 | 6.51 |
| Total moisture and volatile % | 18.36 | 8.45 | 17.58 | 15.82 | 11.48 | 13.83 | 13.48 |
| Residue after ignition % | 81.64 | 91.55 | 82.42 | 84.18 | 88.52 | 86.17 | 86.52 |

## TABLE VII

### Spent Earth Examination—Bleach No. 1 and Blank

| Earth | XL 000 | Georgia Earth | Floridin 200 mesh | Floridin Regular | Pikes Peak | Filtrol Earth | Death Valley | Blank 5 |
|---|---|---|---|---|---|---|---|---|
| Acetone Extract % on original earth | 6.60 | 7.54 | 8.67 | 7.75 | 6.32 | 13.79 | 24.09 | .31 |
| Insoluble Organic Matter adsorbed % | 3.02 | 2.69 | 2.89 | 2.91 | 1.47 | 2.84 | 7.29 | .23 |
| Insoluble Organic Matter % on Original Oil | .45 | .40 | .43 | .44 | .22 | .42 | 1.09 | .03 |
| Total Matter Adsorbed % on the Earth | 9.62 | 10.23 | 11.56 | 10.66 | 7.79 | 16.63 | 31.38 | .54 |
| Total Matter adsorbed % on the Oil | 1.44 | 1.53 | 1.73 | 1.60 | 1.17 | 2.49 | 4.71 | .08 |

## TABLE VIII

### Spent Earth Examination—Bleach No. 2

| Earth | XL 000 | Georgia Earth | Floridin 200 mesh | Floridin Regular | Pikes Peak |
|---|---|---|---|---|---|
| Acetone Extract % on Original Earth | 6.19 | 6.36 | 9.71 | 6.72 | 6.40 |
| Insoluble Organic Matter Adsorbed % | 1.98 | 1.38 | 2.77 | 1.20 | 1.38 |
| Insoluble Organic Matter % on Original Oil | .29 | .20 | .41 | .18 | .20 |
| Total Matter Adsorbed % on the Earth | 8.17 | 7.44 | 12.48 | 7.92 | 7.78 |
| Total Matter Adsorbed % on the Oil | 1.23 | 1.16 | 1.87 | 1.19 | 1.17 |

## TABLE IX

SPENT EARTH EXAMINATION—BLEACH NO. 3

| Earth | XL / 000 | Georgia Earth | Floridin 200 mesh | Floridin Regular | Pikes Peak |
|---|---|---|---|---|---|
| Acetone Extrace % on Original Earth | 4.82 | 7.09 | 7.55 | 6.59 | 6.74 |
| Ignition Loss % on Original Earth | 12.17 | 5.00 | 12.53 | 11.13 | 6.00 |
| Ignition Loss Original Earth % | 8.10 | 3.60 | 10.71 | 9.20 | 5.09 |
| Insoluble Organic Matter Adsorbed % | 4.07 | 1.40 | 1.82 | 1.93 | 0.91 |
| Insoluble Organic Matter % on Original Oil | .61 | .21 | .27 | .29 | .14 |
| Total Matter Adsorbed % on the Earth | 8.89 | 8.49 | 9.37 | 8.52 | 7.65 |
| Total Matter Adsorbed % on the Oil | 1.33 | 1.27 | 1.40 | 1.28 | 1.15 |

## TABLE X

TITRATION OF FULLER'S EARTH SAMPLES WITH FERROUS AMMONIUM SULPHATE SOLUTION

About 10 grams per liter.
Results comparative only.

| | | | |
|---|---|---|---|
| IXL/000 | 24 cc. | Filtrol | 1 cc. |
| Georgia Earth | 2.5 | Death Valley | 1 |
| Floridin No. 975 | 10 | Kieselguhr | 1.50 |
| Floridin XXF | 4 | Pumice Stone | 1.50 |
| Pikes Peak | 1 | Silex Flour | 3 |

# SULFUR-TERPENE SUBSTITUTION COMPOUNDS

BY WILLIAM BEACH PRATT

Read at the Richmond, Va., Meeting, Dec. 7, 1922.

The term "oil" indicates substances differing widely in composition and properties. We have the fixed oils, which are generally glycerides of stearic, palmitic, and oleic acids; also the essential oils, consisting wholly or in part of hydrocarbons or mixtures of hydrocarbons with compounds of carbon, hydrogen, and oxygen. Broadly, the term is used to include also such as are known as mineral oils, which are petroleum hydrocarbons, coal-tar hydrocarbons, and various compounds of these series.

It will only be possible to mention sulfur products of some of these oils in a general survey of the subject. It is the large division of the essential oils, known as the terpenes, to which our work has been directed and with which we have had experience in commercial application.

The particular terpene always associated with sulfur, and on which one of the largest industries of our country has been established, has a well-recognized reaction with sulfur. Nevertheless, little is understood as to the real chemistry of vulcanization in the rubber industry.

It is really remarkable in view of the commercial value in relation to the combining of sulfur with this terpene, rubber, that for so many years the other terpenes had not been investigated in regard to such reaction.

## Connection with Vulcanization

About twelve years ago the interest of our laboratory was directed to this work through the rapidly increasing demand for vulcanizing rubber to fabrics. Attempts had been made under pressure, *in vacuo*, and by every conceivable mechanical device, to more perfectly incorporate rubber-benzene solutions with cotton fabric, in order to give a better bonding with rubber compounds. The colloidal structure of the rubber and the impossibility of securing a penetration even between the fibers of the thread, led to this definite problem—the possibility of constructing a sulfur-terpene

compound, noncolloidal in character, which would be absorbed by the cotton fiber, so that when a rubber compound was placed in contact with the fabric, reaction would occur between the intimately associated sulfur terpene of the fabric and the rubber mass, thereby effecting a union more permanent in relation to the necessary endurance test of commercial use and application.

There has been little published in the literature concerning the combination of sulfur and the liquid terpenes. Because of our work on the vulcanizing of rubber, we drew the conclusion that high temperature and high pressure were essential factors to such reaction. In 1915 we had a bomb constructed in order to carry out a reaction between sulfur and the liquid terpenes at a pressure of 1200 lbs., and carried on experiments for many months with varying pressures and temperatures. We found that, although little had been presented for publication, many of those connected with the technical work of the rubber industry had made similar attempts.

After several years of work the direction of research indicated the use of a simple reflux condenser and the ultimate process and product are now patented.[1]

We had found that the sulfur-terpene product obtained corresponded almost exactly with our ideas of what we were originally working to secure. The especial value was found to be in the treatment of fabric for the manufacture of automobile tires and other rubber articles. Being noncolloidal its solutions penetrated the fibers as we had anticipated, so that they became impregnated with this product and were so strengthened that American peeler cotton thus treated became comparable to the more expensive untreated Sea Island or Egyptian cottons.

The solution of the sulfur-terpene compounds is styled "toron," and the fabric, after impregnation with it, "toron-treated fabric." Experience has shown that rubber may be calendered to toron-treated fabric with much greater ease than to the original gray goods, and that the operation is attended with a complete absence of the skips or blisters which occur in ordinary practice with gray goods. This is due to the fact that the treatment with toron conditions the gray goods so that the surface of the fabric is everywhere uniformly prone to adhesion to and incorporation with the rubber. As a consequence "spreading" becomes unnecessary, and thus the time and expense attending this operation are eliminated. Moreover, the

[1] U. S. Patents 1,349,909 to 1,349,914, inclusive (1920).

"friction," which is the term used in the rubber industry to connote the resistance of the rubber to separation from the fabric, is markedly greater for the toron-treated gray goods than for the same gray goods untreated. Various other advantages in use, such as protection of the tire fabric from contact with air, moisture, and molds, follow such impregnation. But the full effects of these are now the subject of searching investigations.

The fundamental sulfur-terpene compounds themselves have especially engaged the attention of the author, and it is the purpose of this paper to present the more important results so far obtained in the investigation of the products resulting from the reaction of sulfur and turpentine.

## Description of Product

The sulfur-terpene product prepared in the manner described in the first patent of the series referred to above, from sulfur and American oil of turpentine, which consists largely of $\alpha$-pinene, varies physically from a dark liquid or semisolid viscous mass to a black, hard, brittle mass which breaks with conchoidal fracture and presents a vitreous luster on the surfaces of fracture, and in many respects resembles the mineral rubbers. The character of the product obtained depends on the proportions of reacting materials, the temperature, duration of the process, and other conditions of formation.

These products are insoluble in water, but are very soluble in chloroform, carbon disulfide, benzene, toluene, and xylene. The "semisolid" products are also almost entirely soluble in most of the other common organic solvents, but they are very difficultly soluble in ethyl and methyl alcohol. The "hard" products are as a rule considerably less soluble than the others.

Solutions of these sulfur-terpene compounds pass readily through parchment and according to this test are to be regarded as noncolloidal. This conclusion as to the noncolloidal nature of the sulfur-terpene compounds is confirmed by determinations of the depression of the freezing point of pure benzene by several of these compounds.

The sulfur content of the various products varies with the proportions of sulfur and turpentine in the reacting mixture, as well as with the course of the reaction in their formation. Products containing as high as 50 per cent sulfur have been obtained.

Analysis of sulfur-terpene compounds prepared from turpentine which contained less than 0.50 per cent of oxygen has demonstrated the absence of oxygen as a constituent of these compounds, and it has been shown further that the passage of air through the sulfur-turpentine mixture during reaction does not result in the introduction of oxygen as a constituent of the final sulfur-terpene product.

The reaction between sulfur and turpentine is accompanied by the evolution of hydrogen sulfide, and this fact may be taken as proof that the reaction is in part at least one of substitution. But the proportions of carbon, hydrogen, and sulfur in the resultant product, as shown by analysis, are not in harmony with an assumption of substitution alone. Rather, the evidence favors strongly also a simple addition of sulfur to the terpene molecule. Moreover, the results of determinations of apparent molecular weights by the freezing-point method seem to require a further assumption of a reaction involving the condensation of two or more molecules of sulfur-terpene compounds.

Interesting experiments were made to determine the effect of air agitation during reaction. The results show that the passage of air through the reacting sulfur and turpentine did not affect the introduction of oxygen as a constituent of the final product, but it did apparently cause a reduction in the sulfur content of the product.

The experiments were as follows: the turpentine used was a fraction which distilled at 156° to 160° C. and had a refractive index 1.4724 at 23° C. It had the following analysis:

C, 87.78; H, 11.74; O, 0.48 per cent.
$C_{10}H_{16}$ requires: C, 88.24; H, 11.76 per cent.

*Experiment I.*—The turpentine (136 g.) and sulfur (128 g.) were heated for 6 hrs. at approximately 175° C. under reflux condenser, and with constant mechanical agitation. The product of the reaction, A, a dark viscous mass, had the following composition:

| | |
|---|---|
| Carbon | 51.34 per cent. |
| Hydrogen | 5.90 per cent. |
| Sulphur | 42.86 per cent. |

Ratio C : H : S = 3.2 : 4.4 : 1.0

*Experiment II.*—This experiment was carried out exactly as the preceding, except that throughout the operation a slow current of

air was allowed to bubble through the reacting mass. The product, B, of this experiment was somewhat more viscous than A. It had the following composition:

Carbon.....56.80 per cent.
Hydrogen..... 5.82 per cent.
Sulfur.....37.50 per cent.
Ratio C : H : S = 4 : 5 : 1

## Distillation of the Sulfur-Terpene Products in Partial Vacuum

*Product A (without air treatment).*—A sample (31 g.) of A was subjected to fractional distillation under a pressure lying between a maximum and minimum of $2^3/_8$ and $1^7/_{16}$ in., respectively. The distillates were condensed in receivers cooled to about −10° C. The temperature of the heating bath of oil was raised slowly to 155° C. At this temperature there was a decided break in the distillation, and the succeeding fraction did not distil until a temperature of 180° C. was reached. The operation was continued up to a maximum of 214° C. The distillation at the higher temperatures was no doubt accompanied by considerable decomposition, as evidenced by the very disagreeable odor of escaping gases or vapors and by the deficiency in weight of the total fractions.

The results are shown in Table I.

TABLE I

Product A

| | Weight G. | Description | Index of Refraction at 18° C. | Composition Per cent | | |
|---|---|---|---|---|---|---|
| | | | | C | H | S |
| Fraction 1, up to 155° C..... | 1.8 | Light yellow liquid, smelled of turpentine mixed with sulfur compound | 1.4694 | 85.55 | 10.93 | 3.52 |
| Fraction 2, 180°–214° C..... | 2.2 | Red liquid, disagreeable odor, faint turpentine odor | 1.5587 | 68.61 | 8.35 | 23.04 |
| Residue..... | 20.0 | Hard, brittle mass.... | ..... | 51.62 | 4.60 | 43.78 |
| Loss..... | 7.0 | | | | | |

TABLE II

PRODUCT B

| | Weight G. | Description | Index of Refraction at 18° C. | Composition Per cent | | |
|---|---|---|---|---|---|---|
| | | | | C | H | S |
| Fraction..... | 2.0 | Similar to Fraction 1 of Product A | 1.4784 | 84.51 | 10.68 | 4.81 |
| Residue..... | 46.0 | Stiff, viscous mass | ..... | 55.22 | 5.57 | 39.21 |

It thus appears that the sulfur-terpene product A contained about 6 per cent of unattacked turpentine which could be removed by distillation. By making due allowance for the effect of Fraction 1 on the original analysis of Product A, by calculation we obtain the corrected analysis of the sulfur-terpene product A: C, 49.16; H, 5.57; S, 45.27 per cent.

If we assume that this substance is a pure, individual compound which is, however, unlikely, and that it contains the same number of carbon atoms as the original terpene from which it was derived, or a multiple of the same, we may write its empirical formula most closely in accord with analysis as $C_{20}H_{27}S_7$.

*Product B.*—The maximum temperature of the bath during the distillation of a sample of B (48 g.) was 156° C., and the contents of the distilling flask reached a maximum of 130° C. The pressure varied from $1^1/_4$ to $1^1/_{16}$ in. Only one fraction was removed. The results are shown in Table II.

There was no evidence of any decomposition during the distillation.

From an analysis of the residue the empirical formula $C_{20}H_{24}S_5$ may be derived.

### COMPOSITION OF A TYPICAL "HARD" SULPHUR-TERPENE COMPOUND

This compound was prepared from equal parts by weight of ordinary turpentine and sulfur. The operation was conducted at a comparatively low temperature for approximately 90 hrs., after which time the reaction was completed at about 170° C. At the end of the operation, at 170° C., the product was so stiff that it could no longer be stirred, and it showed no tendency to flow. On cooling it became a hard, brittle mass, which for convenience of reference we shall designate as "C."

TABLE III

| Substance | Formula | Composition Per cent | | | | Weight of Sample | Weight of Solvent | Undercooling (Mean of 2 Observations) | Depression F. P. (Mean of 2 Observations) | Depression of F. P. by 1 G. Sub. in 100 G. Solvent | Apparent Molecular Weight | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | H | S | O | G. | G. | ° C. | ° C. | ° C. | | |
| $B_1$ (before distillation) | $C_{20}H_{24}S_5$ | 56.80 | 5.82 | 37.50 | .... | 0.4604 | 26.4954 | 0.323 | 0.257 | 0.1474 | 339.3 | 344.4 |
| | | | | | | 1.1830 | 26.8366 | 0.613 | 0.635 | 0.1430 | 349.5 | |
| $B_2$ (after distillation) | | 55.22 | 5.57 | 39.21 | .... | 0.4176 | 20.4902 | 0.191 | 0.277 | 0.1356 | 368.7 | 375.3 |
| | | | | | | 0.2300 | 23.0264 | 0.47 | 0.1315 | 0.1310 | 381.8 | |
| C | $C_{20}H_{24}S_8$ | 46.14 | 4.33 | 47.80 | 1.73 | 0.3980 | 19.2274 | 0.125 | 0.223 | 0.1075 | 464.8 | 457.3 |
| | | | | | | 0.2414 | 20.0012 | 0.21 | 0.1345 | 0.1112 | 449.8 | |

Analysis of C

| | Per cent |
|---|---|
| Carbon | 46.14 |
| Hydrogen | 4.33 |
| Sulfur | 47.80 |
| Oxygen (by difference) | 1.73 |

The small proportion of oxygen was very probably derived from the oxygen of the crude turpentine used. Reducing this analysis to an oxygen-free basis, we have: C, 46.96; H, 4.41; S, 48.63 per cent.

This composition corresponds very closely to that of a compound of empirical formula $C_{10}H_{12}S_4$ or $C_{20}H_{24}S_8$.

## Depression of the Freezing Point by Solutions of Sulfur-Terpene Compounds

These determinations were made in the usual manner for molecular-weight determinations by the freezing-point method, with the Beckmann apparatus, using pure benzene as solvent. The substances examined and the results are shown (Table III).

The results of these determinations show that the depression of the freezing point of benzene by the sulfur-terpene compounds is proportional to concentration; and, furthermore, the values obtained by calculation of molecular weights from the freezing-point data are of such magnitude as one should expect in the case of non-colloidal substances.

The molecular weight as determined for $B_2$ (375) is somewhat lower than that required for a compound $C_{20}H_{24}S_5$ (424). This is true also in the case of C, where the determined value is 457 as against 520 required for $C_{20}H_{24}S_8$. But only an approximation to agreement was to be expected, as in neither case was the substance supposed to be a single pure compound. However, in both instances, the results indicate condensation of terpene molecules along with the introduction of sulfur.

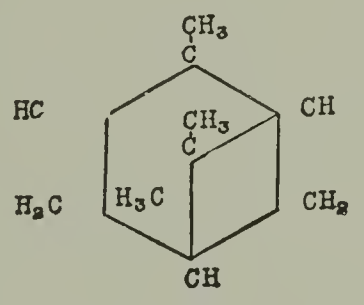
## Discussion

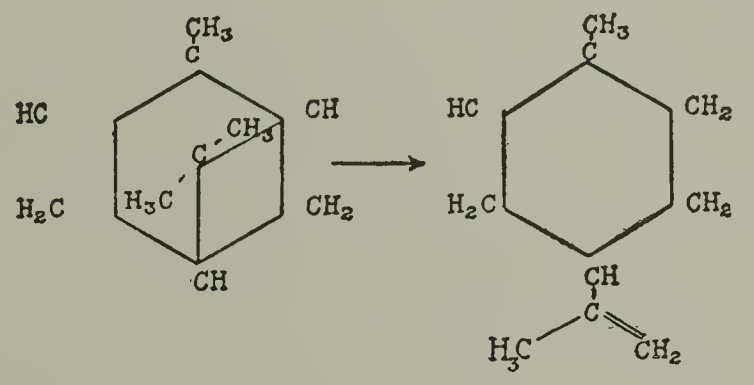
It must be recognized that the reactions between sulfur and turpentine may be and most likely are very complicated, and that the resultant sulfur-terpene products are in consequence very probably mixtures of considerable complexity. For this reason any attempt at the present stage of our investigation to represent by equations

and formulas the course of reactions and the constitution of the sulfur-terpene products can be only speculative. If we were dealing here with a pure terpene, the problem would be in large measure simplified. However, since the turpentine employed consists largely of $\alpha$-pinene, we may assume the reactions in the main to be those between pinene and sulfur, and on this assumption several interesting possibilities are at once suggested. We may consider one such possibility.

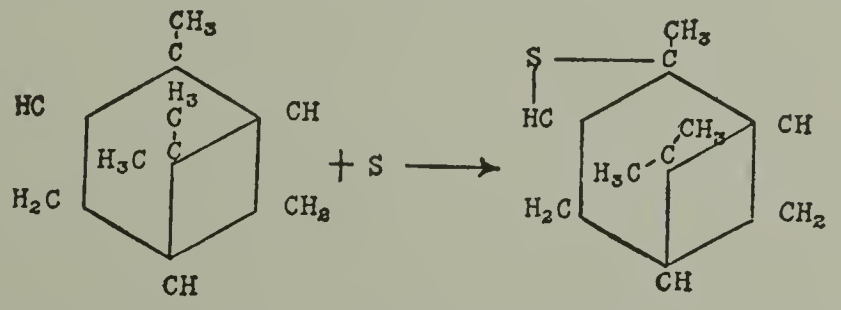
As previously stated, tne results of our experiments show not only substitution and simple addition in the terpene molecule, but also some kind of condensation of molecules.

Assuming the Baeyer picean-ring representation of the constitution of $\alpha$-pinene,[2] we should expect the addition of one atom of sulphur at the position of the double bond. The possibility of the addition of a second sulfur atom is suggested by the ready intramolecular rearrangement of the pinene molecule so commonly observed, wherein dipentene, containing two double bonds, is derived from pinene.[3]



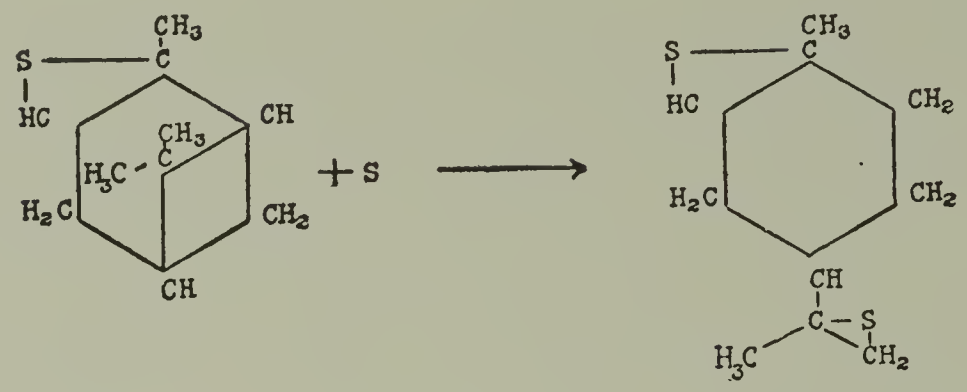

Assuming, therefore, the addition of two atoms of sulfur to one molecule of pinene, we may express this action in two stages:



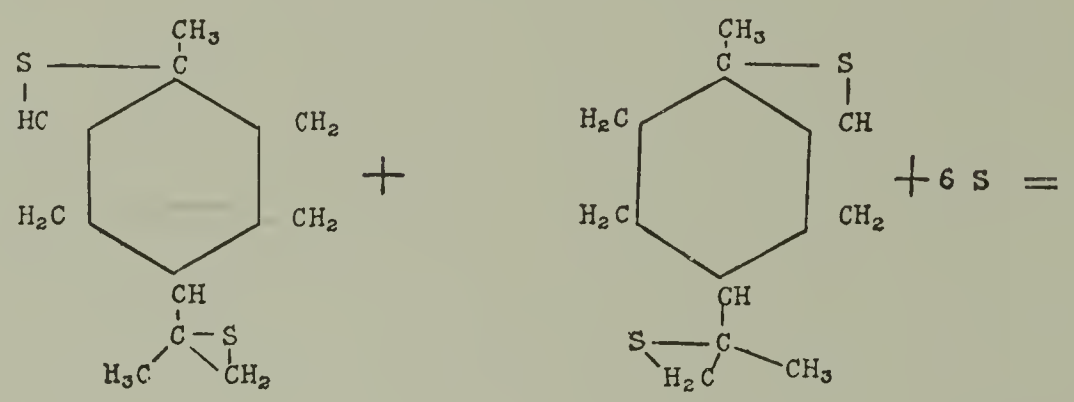

The addition of the second atom of sulfur may be represented as accompanied by molecular rearrangement as follows:

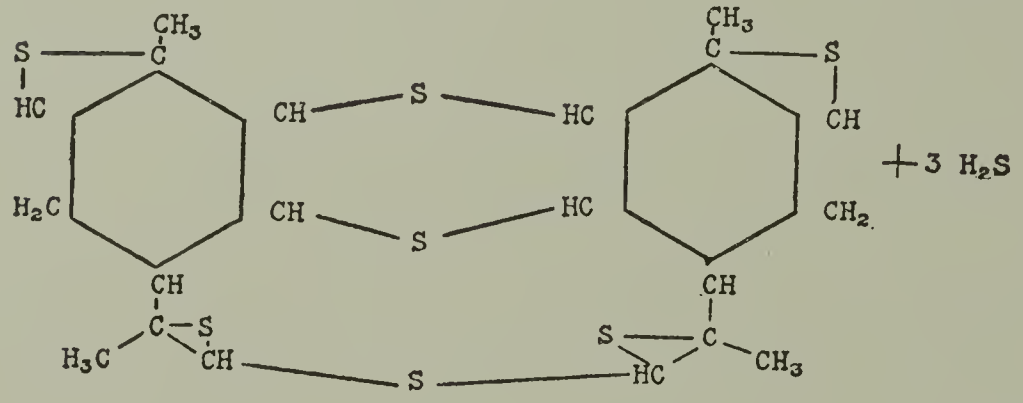
[2] *Ber.*, **29** (1896), 2779.

[3] Wallach, "Terpene und Camphor," **1914**, 15.



The formation of a compound of the composition $C_{20}H_{26}S_7$ from the above $C_{10}H_{16}S_2$ by substitution of sulfur might then be represented in the following manner:





Some such explanation as this may be applicable to the formation and structure of the sulfur-terpene product A, described above, and having the composition represented by the empirical formula $C_{20}H_{27}S_7$, and with such modifications as may be required in each case, to the other products.

## The Action of Sulfur on Organic Compounds. Some Typical Examples

One of the oldest examples of the action of sulfur on organic substances is the well-known method of preparing hydrogen sulfide by the fusion of paraffin with sulfur, which appears to involve the formation of more condensed hydrocarbon molecules from which

hydrogen has been partially removed in combination with sulfur.[4] And in the field of the dyes [5] we have that large class of substances known as the sulfur dyes, many of which are the result of the direct action of sulfur. The reactions involved in the formation of these dyes are doubtless in most cases quite complex, but in numerous instances they are well established as consisting essentially in the addition or substitution of sulfur, usually accompanied by the evolution of hydrogen sulfide, and the conjugation of two or more molecules through sulfur. Furthermore, the role of sulfur in the formation of natural and artificial asphalts [6] is very generally recognized as an important one and as involving the condensation and polymerization of organic materials to form products which may or may not contain sulfur as a constituent. For instance, according to Winkler [7] artificial coal-tar asphalt can be greatly improved by heating with about 5 per cent of sulfur until the evolution of hydrogen sulfide ceases, whereby a molecular condensation takes place, with removal of hydrogen and the formation of a more difficultly fusible residue. Very similar products are the well-known wood cement of Häusler [8] prepared from coal tar, pitch and sulfur, and the sulfur-tar or benz-asphalt,[9] made by boiling two parts of sulfur in three parts of coal tar.

Many other such examples of the action of sulfur on organic compounds are to be found in the literature, and we give below a bibliography which we believe is representative of the literature regarding those compounds whose reaction with elementary sulfur has been investigated.

### Bibliography

**Turpentine:** Lange "Die Schwefelfarbstoffe," 14; Winkler, *Chem. Zentr.*, **29** (1858), 337.

**Ethylene:** Meyer and Sandmeyer, *Ber.*, **16** (1883), 2176.

[4] Clarke, "Data of Geochemistry," *U. S. Geol Survey, Bull.* **330** (1908), 627, footnote.

[5] Lange, "Die Schwefelfarbstoffe, ihre Herstellung and Verwendung;" Nietzki, "Chemie der Organischen Farbstoffe;" Cain and Thrope, "The Synthetic Dyestuffs, etc.;" Wahl and Atack, "The Manufacture of Organic Dyestuffs."

[6] Köhler, "Die Chemie und Technologie der Näturlichen and Künstlichen Asphalte," **1913**.

[7] *Chem. Zentr.*, **29** (1858), 337.

[8] *See* Nöthling, "Der Asphalte," 192.

[9] *Wagner's Jahresber.*, **1860**, 554.

**Acetylene:** Meyer and Sandmeyer, *Loc. cit.*; de Coninck, *Bull. sci. acad. roy. Belg.*, **1908**, 303; *C. A.*, **3** (1909), 643; Capelle, *Bull. soc. chim.*, [4] **3** (1908), 150; *C. A.*, **2** (1908), 1562.

**Styrene:** Baumann and Fromm, *Ber.*, **28** (1895), 890.

**Stilbene:** Baumann and Klett, *Ibid.*, **24** (1891), 3310; cf. *Ann.*, **38** (1841), 320.

**Benzene:** Renard, *Bull. soc. chim.*, [3] **6** (1891), 194; Merz and Weith, *Ber.*, **4** (1871), 394.

**Toluene:** Renard, *Bull. soc. chim.*, [3] **4** (1890), 958; *Ibid.*, **5** (1891), 278; Lange, "Die Schwefelfarbstoffe," 24.

**Dibenzyl:** Szperl and Wierusz-Kowalski, *Chem. Zentr.*, **89** (1918), 908; abstract of *Chem. Polski*, **15** (1917), 19.

**Naphthalene:** Merz and Weith, *Züricher Chem. Harmonika; Ber.*, **2** (1869), 341 (*see* Lange, "Die Schwefelfarbstoffe").

**Anthracene:** Badische Anilin und Soda Fabrik, D. R. P. 186,990.

**Indene, hydrindene, and cyclopentadiene:** Friedmann, *Ber.*, **49** (1916), 50; *C. A.*, **10** (1916), 896; *Ber.*, **49** (1916), 683; *C. A.*, **10** (1916), 2712.

**Aniline:** Merz and Weith, *Züricher Chem. Harmonika; Ber.*, **2** (1869), 341 (*see* Lange, "Die Schwefelfarbstoffe"); Kraft, *Ber.*, **7** (1874), 385, 1164; Kehrmann and Bauer, *Ibid.*, **29** (1896), 2363; Hofmann, *Ibid.*, **27** (1894), 2806, 3320.

***p*-Toluidine:** Merz and Weith, *Ber.*, **4** (1871), 393; D. R. P. 34,299; Truhlar, *Ber.*, **20** (1887), 664; Dahl and others, D. R. P., 35,790; Jacobson, *Ber.*, **22** (1889), 333; Gattermann, *Ibid.*, **22** (1889), 424; **25** (1892), 1084; cf. Anschütz and Schultz, *Ibid.*, **22** (1889), 581; Green, *Ibid.*, **22** (1889), 969.

***m*-Tolylenediamine:** Cassella and Co., D. R. P. 139,430 and D. R. P. 152,595; Schultz and Beyschlag, *Ber.*, **42** (1909), 743; *C. A.*, **3** (1909), 1176.

**Diphenylanime:** Bernthsen. *Ann.*, **230** (1885), 77.

**Benzanilide (phenylbenzamide):** Hofmann, *Ber.*, **12** (1879), 2360; **13** (1880), 1223; Lange, "Die Schwefelfarbstoffe," 18.

**Tetramethyldiaminodiphenylmethane:** Nietzki, Chem. d. org. Farbs.

**Cinnamic Acid:** Baumann and Fromm, *Ber.*, **28** (1895), 891.

**Benzyl alcohol, diphenylcarbinol, dibenzyl ether, and diphenylcarbinol ether:** Szperl and Wierusz-Kowalski, *Chem. Zentr.*, **89** (1918), 909; abstract of *Chem. Polski*, **15** (1917), 23.

**Phenol:** Möhlaus and Seyde, *Chem.-Ztg.*, **31** (1907), 937.

COMMERCIAL AND SYNTHETICAL LABORATORY,
NEWTONVILLE, MASS.

## DISCUSSION

DR. CHAS. L. REESE: I should like to know if you have done any work on combinations of rosin and sulphur.

MR. PRATT: We have, and we have in addition gone through those oils characterized as rubber oils. It is possible to treat rosin and from it to produce a product which corresponds almost exactly to turpentine. But the treatment of rosin with sulphur produces, within, say, the first half hour of reaction, an absorption of the sul-

phur in the mass, and an odor which is simply beyond description; not $H_2S$, but sulphur compounds of the vilest kind and acid products, of which, when you apply steam distillation, you can make nothing whatsoever because the sulphur breaks in, combining in so many ways.

DR. REESE: When I first went into the explosives business, sulphur was used in the composition of gelatine dynamite. Mr. Penniman, of the old Atlantic Dynamite Company invented a substitute for sulphur, called vulcanized rosin, and we used it for years in gelatine dynamite as one of the combustibles, because it was believed that it gave a gelatine dynamite which would keep longer.

MR. PRATT: But in making that you did not bring it up to the high temperature where it would combine with sulphur?

DR. REESE: Yes, and it made a very fine, clean, solid product which would grind very easily.

MR. PRATT: I cannot give you the temperatures used in that regard, but by combining the sulphur with the rosin and heating the mixture, it will give a very definite mass, and we were trying to carry that on to get a definite reaction from the sulphur.

MR. JOHN M. WEISS: One thing I have noted that Mr. Pratt said about the combination of sulphur and coal tar pitch. I think there are a number of patents that cover combinations of sulphur with tar and pitch, but I may say in all our experience we have never found that a usable product was obtained from coal tar products in that way. Hydrogen sulphide is given off and a very hard mass, brittle and useless, results.

MR. JEROME ALEXANDER: Just two points. Sulphur in itself in various physical forms has very curious properties, and it is not always necessary to postulate sulphur compounds in order to postulate these properties. For example, von Weimarn some years ago heated sulphur until it assumed its second fluid condition, and then chilled it in liquid air. He got a transparent rubber-like mass which became brittle as it crystallized. Phosphorus in certain curious forms also has properties quite different from those of its ordinary forms. P. W. Bridgman took ordinary phosphorus and by simply compressing it at high pressures, produced a new form of hard black phosphorus which conducts electricity. Mr. Pratt seems to believe that colloids do not diffuse. Most colloids diffuse slowly, a fact recorded by Thomas Graham.

PRESIDENT HOWARD: I should like to ask Mr. Pratt regarding

the slide showing the atoms of sulphur, concerning the evidence on which that formula rests. Is that isolated as a definite compound, and has its weight been determined?

MR. PRATT: It has. That has been checked, and that is the standard product having seven atoms of sulphur. It has been checked a great many times. Insofar as we are able to control the reaction in a laboratory way, it should be very definite. I think you understand what I mean by controlling the reaction, the refluxing, the passage of air through the sulphur, with definite range of temperatures for a definite time. And there is always the possibility of certain errors, but they have been checked down so that it is very reasonable to suppose that we have a definite compound.

PRESIDENT HOWARD: Does the molecular weight check?

MR. PRATT: Yes, and very surprisingly so if we consider the possibility of various compounds. It is surprising that it checks as closely as it does. In the alternate of carrying on of the reaction to the final product, it was almost the hope and we anticipated that we would have little sulphur, but the interesting thing is that the sulphur works down to a point just before the complete decomposition where it can be plotted perfectly between the combined molecular weights of the series.

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